Volume 38 August, 1934 Number 2

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

Contents

Eilhard Alfred Mitscherlich. To the Sixtieth Birthday of the German Investigator. E. Von Boguslawski 83
Root Habits of Certain Crop Plants as Observed in the Humid Soils of New Jersey. Nolan F. Farris 87
Application of the Theory of Probability to the Size Distribution of Soil Aggregates. Clark Affleck 113
The Carbon-Nitrogen Ratio in Relation to Soil Classification. M. S. Anderson and Horace G. Byers 121
A Rapid Method for the Determination of Total Nitrogen in Soil. E. M. Emmert 139
Newer Aspects of Nitrification: I. G. Gopala Rao 143
Laws of Soil Colloidal Behavior: XV. Ionic Exchange with Hydroxides. A. J. Pugh 161

Published Monthly by THE WILLIAMS & WILKINS COMPANY
MT. ROYAL AND GUILFORD AVENUES, BALTIMORE, MARYLAND, U. S. A.

Made in United States of America

SOIL SCIENCE

FOUNDED BY
RUTGERS COLLEGE
NEW BRUNSWICK, N. J.

ADVISORY STAFF

A. W. Blair, J. S. Joffe, L. L. Lee, H. C. McLean, G. T. Nightingale, A. L. Prince, J. W. Shive, H. B. Sprague, R. L. Starkey, and S. A. Waksman, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

F. J. ALWAY
University of Minnesota, St. Paul, Minn.

K. ASO
Imperial University, Tokyo, Japan

C. BARTHEL
Lantbrukshögskolan, Uppsala, Sweden

P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa

B. C. BURT
Imperial Council of Agricultural Research, New Delhi, India

H. J. CONN
New York State Experiment Station, Geneva, N. Y.

ALBERT DEMOLON
Ministry of Agriculture, Paris, France

E. B. FRED
University of Wisconsin, Madison, Wis.

V. V. GEMMERLING
Agronomitcheskii Institute, Moskovskii Universitat, Moscow, U. S. S. R.

J. E. GREAVES
Utah Agricultural College, Logan, Utah

ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium

B. L. HARTWELL
26 Rowe St., Auburndale, Mass.

D. J. HISSINK
Soil Science Institute, Groningen, Holland

O. LEMMERMANN
Institut für Agrikulturchemie u. Bakteriologie der Landwirtschaftlichen Hochschule, Berlin-Dahlem, Germany

C. B. LIPMAN
University of California, Berkeley, Calif.

BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.

HENRIK LUNDEGÅRDH
Centralanstalten för jordbruksförsök, Stockholm, Sweden

T. L. LYON
Cornell University, Ithaca, N. Y.

M. M. MCCOOL
Boyce-Thompson Institute, Yonkers, N. Y.

W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.

S. MATTSON
Lantbrukshögskolan, Uppsala, Sweden

E. A. MITSCHERLICH
University of Königsberg, Prussia

C. A. MOOERS
University of Tennessee, Knoxville, Tenn.

D. H. PRIANISHNIKOV
Petrovsko-Rasumovskaia Akademia, Moscow, U. S. S. R.

THEO. REMY
Institut für Boden- und Pflanzenbaulehre, Bonn a. Rh., Prussia

G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy

E. J. RUSSELL
Rothamsted Experimental Station, Harpenden, England

O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.

ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary

J. STOKLASA
Technical High School, Prague, Czechoslovakia

CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio

N. M. TULAIKOV
Agricultural Experiment Station, Saratov, U. S. S. R.

G. WIEGNER
Landwirtschaftliche Hochschule, Zürich, Switzerland

S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter, May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.

Copyright, 1934, The Williams & Wilkins Company

EILHARD ALFRED MITSCHERLICH

To the Sixtieth Birthday of the German Investigator

E. VON BOGUSLAWSKI[1]

Königsberg University

The name of Eilhard Alfred Mitscherlich has long been known through the literature and research institutions the world over. His methods of pot experiments and plant physiological approach to soil science have been fundamental in investigating "the law of physiological relations," on which the determination of the fertilizer requirements of the soil hinges. He is known for his methods of establishing compensating factors in field experiments and of determining heat of wetting, hygroscopicity, and climatic factors associated with evaporation, and for many other important concepts. His sixtieth birthday, on August 29, 1934, offers an occasion to sum up some of the important details of his life and work and to point out further particulars which cannot be communicated by a mere enumeration of papers.

In choosing a scientific profession, E. A. Mitscherlich followed his family's tradition. His father, Alfred Mitscherlich, was a physician and professor of the University of Berlin. His grandfather, Eilhard Mitscherlich, professor in Berlin, was the well-known chemist who contributed so much to our knowledge of organic chemistry and who devised the first polarimeter for use in sugar chemistry.

E. A. Mitscherlich studied chemistry and physics in Kiel and began his scientific work in agriculture as Rodewald's assistant. He received the degree of doctor of philosophy for his work "The evaluation of the physical properties of the soil by means of its heat of wetting." This work contains an important and original method in soil science. At the same time, by determining the soil surface, Mitscherlich introduced one of the main problems of general soil science. He was, however, chiefly interested in the physical properties of soil, in a way similar to Wollny and his co-workers and the school of Ramann. In Rodenwald's Institute he published his habilitation work "Investigations on the physical properties of soil." Even these first papers give evidence of what was to become, in course of time, one of his greatest contributions to the field of soil science: his severe and uncompromising scientific attitude. Mitscherlich, with his abundant energy, opened a fertile new field in soil science. For the younger generation, the principles of his work and his productivity both in theory and experiment are most impressive. There is scarcely a problem of general plant culture left unattacked during the first ten years of his research work.

[1] Translated from the German by S. A. Waksman.

In 1903 he published with Rodewald the method of hygroscopicity, and in the same year his first papers on the mathematical treatment of experimental results. In 1904, he constructed (independent from Livingston) his first atmometer. In the years 1907 to 1911, he did his fundamental work on the chemical methods of analysis. This was done in Königsberg, to which he had been called, as head of the Pflanzenbau Institut, in 1907. In the same year he received a call to Pasoeroean (Java), which he refused.

The outstanding difference between Mitscherlich and his colleagues in all of his activities was his original method of choosing problems in soil science. His idea was that the principal task of the science is the examination of the growth factors. This was not completely new, but it was essential for limiting the nature of the problem and the methods adopted and for the evaluation of the results.

In the first edition of his "Soil Science for Agriculturists and Foresters" (Bodenkunde für Land- und Forstwirte, 1905), in which he summarized anew his ideas of plant growth, he definitely started out on a new path distinct from geological soil science. He realized, for instance, that by extracting phosphoric acid from the soil one cannot learn about the processes that take place between the plant and the phosphoric acid in the soil. So he preferred to study the effect of the phosphoric acid in soil by means of the growing plant itself. He let the plant give the answer to the effect of phosphoric acid during the vegetation period.

He refuted Liebig's idea that the growth of plants depends mainly on the minimum factor, and conceived the crop yield as a product of the joint action of all the factors combined. For the most important hitherto known chemical and climatological growth factors he was able to confirm his inductive assumption that the crop yield approaches a maximum asymptotically with the increase of one factor. Independent of the maximum of the latter, the increase in crop yield differs only quantitatively and follows, for the same factor, the law of the constancy of the so-called "growth-factor."

The first investigations of "The law of action of the growth factors" were carried out in Kiel. In Königsberg, he, together with his collaborators, accumulated for a period of 20 years an extensive mass of experimental data. Beginning with his scientific data, Mitscherlich utilized pot experiments for determining the fertility of the soil, so important for practical agriculture.

In 1923, the first edition of this book "The Determination of the Fertilizer Requirement of the Soil" appeared. Here, the methods of field experiments and pot experiments are compared, and the possibility is elucidated of drawing conclusions from pot experiments as applied to soil problems.

This practical utilization of his scientific results and the latter as well met with severe criticism from his colleagues, especially in his home country. A scientific fight began concerning the constancy of the "growth factor." It remained, for the time being, a fight for concepts, the exact limitation and sensitivity of all known methods not offering any counter proof.

On the basis of his own experiments, Mitscherlich can best judge for himself to what extent he has succeeded in eliminating individual factors from the factor complex. Especially recently, Mitscherlich has pointed out repeatedly that some physicochemical and chemical methods might also prove useful for the separation of the factor complexes, with special reference to the soil solution and to the surface of soil particles. He himself is now working in this direction.

Mitscherlich is highly esteemed in cultural and civil life and fulfills many honorary functions in many scientific societies. More than a hundred pupils have left his institute during the last 28 years. Four times he was Rektor of the University. Since 1922, he has been Director of the Agricultural Institute of the University. He is a co-editor (with Mez) of the *Botanisches Archiv* and of the *Biologe*, a collaborator of SOIL SCIENCE and the Russian Journal *Pedology*, and is a member of several local and foreign scientific academies. He has been for years President of the Fourth Commission of the International Society of Soil Science.

ROOT HABITS OF CERTAIN CROP PLANTS AS OBSERVED IN THE HUMID SOILS OF NEW JERSEY[1]

NOLAN F. FARRIS[2]

New Jersey Agricultural Experiment Station

Received for publication August 28, 1933

During recent years considerable attention has been directed to the study of the root systems of various agricultural plants. These studies have not been prompted entirely by curiosity, even though earlier studies were begun in that manner. Later investigators have two objects in view: (*a*) to seek improvements in varieties and strains of crop plants, and (*b*) to account for the behavior of plants under different environmental conditions.

Many methods are used to improve the yield and quality of crops: Fertilizers are applied in large amounts; green manures are used to add organic matter to the soil; soil acidity is corrected by the use of lime; and the soil is kept in excellent tilth by proper and judicious cultivation. Still, in many cases, farmers are disappointed because of failure to increase yields or improve quality. The plants may be of the best approved variety, but just as a chain is as strong as its weakest link, so a plant yields in accordance with the ability of its root system to supply it with water and nutrients. It is only recently that attempts have been made to improve crops by developing varieties with superior root systems, or by so changing the soil conditions that the root systems will become more efficient. It would seem that this line of attack offers great possibilities.

Other workers have been interested in root development as a means of explaining the behavior of the same species of plants under different environmental conditions. It is evident that the differences must be manifested, either directly or indirectly, through the roots.

Heretofore, most of the root investigations have been made in the semi-arid or sub-humid sections of the western and midwestern states. These soils, which have been described by Wolfanger (43), are called "Pedocals." The fertility of these soils, in general, is high and they present no unusually difficult problems in cultivation or management.

The humid soils ("Pedalfers") of the eastern states, on the other hand, are much older soils and have been formed under different environmental condi-

[1] Part of a thesis submitted in partial fulfillment of the requirements for the degree of doctor of philosophy at Rutgers University, New Brunswick, New Jersey.

Journal Series paper of the New Jersey Agricultural Experiment Station, department of agronomy.

[2] Research assistant in agronomy.

tions. The natural fertility is usually low, and the low organic matter content influences the soil texture and structure to such an extent that, in many cases, cultivation and management are extremely difficult.

It is reasonable to expect that different soil factors have a marked influence on the root systems of plants, but very little work has been done in comparing root systems in the humid soils with those in the drier and younger soils. Hence, it has been the purpose of this study to investigate the root development of plants in relation to the factors encountered in the humid soils of New Jersey.

The literature of the subject has been extensively reviewed by Miller (24), and Weaver has compiled extensive bibliographies in his books, "Root Development of Field Crops" (41) and "Root Development of Vegetable Crops" (42). Other researches will be referred to in the discussion of observations and results in this paper.

EXPERIMENTAL METHODS

The crops chosen for investigation were corn, white potatoes, and red clover. These crops represent three distinct types of root systems. Red clover possesses a well-developed tap-root system under most conditions. Corn is recognized as a coarse feeder, and its numerous fibrous roots spread farther laterally and penetrate deeper than those of the potato. The potato plant has a more or less superficial root system.

The direct method of root examination, as developed and described by Weaver (41), was used in these investigations. This method is more desirable than the washing method used by earlier investigators.

To simplify the drawings as much as possible only the main roots and their larger branches were plotted. If the degree of branching was unusual this fact was recorded at the time of observation. In some instances only part of the root system was recorded, in order to simplify the drawings. In such cases it was assumed that the horizontal root extent was the same on all sides of the plant. The volume of soil occupied by roots was calculated on this basis. In the case of mature potato plants the entire root system was plotted, but it appears in two separate drawings. The roots extending at right angles to the row of plants are termed "lateral" and those parallel to the row are called "longitudinal."

The root systems of each crop were examined two or three times during the season, the last examination being at maturity in the case of corn and potatoes. Several plants under each treatment were examined and, as near as possible, a representative plant was chosen for root tracings.

At the time of observation samples of soil were taken near each plant studied and at different depths so as to include all soil horizons or layers in which root growth occurred. The majority of soil samples were taken at 4 and 14 inches. In a few cases samples were taken at 21 inches. These samples were air-dried for storage and later subjected to various chemical and physical tests to

determine what relations might exist between soil conditions and root growth.

At the time the soil samples were taken, volume weight samples were obtained with the Lebedev volume weight sampler (19). The moisture content and pore space of the soils were then calculated from these samples according to the method described by Lyon and Buckman (20).

The following physical and chemical tests were made on the air-dried soil samples: (*a*) the pH values, as determined by the potentiometer and quinhydrone electrode; (*b*) the organic matter content, by the Degtjareff method (13); (*c*) the readily available phosphorus, as described by Truog (38); (*d*) the rough quantitative nitrogen content, using the spot plate test devised by Morgan (25); (*e*) the available potassium, by the Bray method (3); and (*f*) the mechanical analysis, by the hydrometer method of Bouyoucos (2).

RESULTS AND OBSERVATIONS

Weather

It is well known that the weather conditions occurring immediately before and during the growing season have a marked effect on plant growth. The root systems are also affected, although in many instances the effects on this part of the plant are not so noticeable as those on the above-ground parts. However, a small change in the root system may manifest itself to a marked extent in the vegetative portions of the plant. Outside of photosynthesis and damage by wind, hail, and sun-scalding, which affect the aerial portions of the plants directly, climatic factors operate almost entirely through the root systems.

Figure 1 shows the conditions of temperature and rainfall at 5-day intervals during the months of April to September in both 1930 and 1931. These months include practically the entire growing season of each of the three crops.

The weather of 1930 was characterized by temperatures above normal and a total rainfall considerably below normal. Except for the month of June the condition was one of persistent dryness and almost continuous warmth. June was the only month with more than normal rainfall.

The year 1931 was the warmest on record (47 years) and the second driest. However, the rainfall was concentrated in the important part of the growing season from March to August, inclusive, and the distribution was, in general, more favorable. The mean temperature was above normal for every month, with July and September having the greatest departures during the growing season. Thus the season of 1931 was more favorable for crop production than was that of 1930.

Effects of soil conditions on normal root development of potatoes

The root system of the potato plant is more superficial than that of many crops such as corn, wheat, and most legumes. In Nebraska, Weaver (41) found that the roots extend horizontally to a distance of 1 to 2 feet or more and then turn more or less abruptly downward and penetrate the second or third foot of

soil. Branching is profuse throughout the root extent. The branches, however, tend to be relatively short. Weaver states that both depth of penetration and lateral spread, as well as abundance and length of branches, are greatly modified by differences in the water content and fertility of the soil.

The plants which Weaver studied were grown in a mellow loess soil and received no cultivation. The ones investigated in this study were grown on Sassafras loam and received the average cultivation. Sassafras loam is classed by Wolfanger (43) as a gray-brownerth in the Pedalfer group. It consists of a brown loam underlaid at 8 to 10 inches by yellowish brown clay loam which passes into an orange or reddish yellow friable sandy clay. Usually the lower subsoil is more sandy than the upper subsoil. The soil on which part of these tests were conducted had not been cropped for several years, and a rather heavy stand of redtop and bluegrass was turned under at the time of plowing.

The most striking feature of this study was the failure of the potato plants

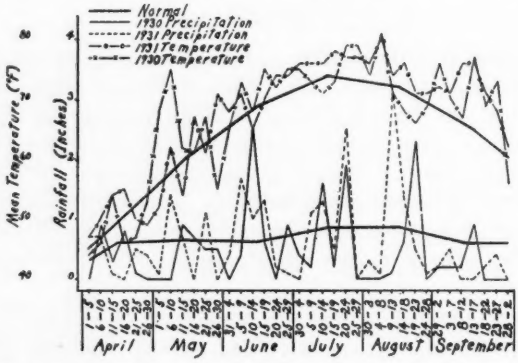


FIG. 1. RAINFALL AND MEAN TEMPERATURES BY 5-DAY PERIODS DURING THE GROWING SEASON IN 1930 AND 1931

to develop extensive root systems. In only a few of the plants examined did the roots penetrate lower than 10 inches.

The root systems of the potato plants had apparently almost reached their maximum development at 70 days after planting. Reference to the illustrations will show that the root systems of the mature plants (110 days old) are only slightly larger than those of the 70-day-old plants.

There was some evidence of root pruning from cultivation but the plants seemed to be able to regenerate these roots at a sufficiently rapid rate to insure vigorous development. Examination of the longitudinal roots, which were not injured by cultivation, shows that there is very little difference between the root systems of the 70-day-old plants and the mature plants. There is no evidence in these studies, however, to show whether different methods of cultivation would improve the plants through increased root development. Such studies have been made but they were carried out on different soils.

In general, then, the average root systems of potatoes studied in this problem were markedly reduced as compared with those reported by previous investigators. The reasons for these differences must therefore be sought by examinations of the climatic and soil conditions under which the studies were conducted.

The potato plant requires a relatively large amount of water for the best development. The best root development is obtained when the plant receives small applications of water just often enough to maintain continuous growth. Thus, it is found that the greatest yields of potatoes have been obtained under irrigation. This may be explained by the fact that the root systems are stimulated to the highest degree and a greater and more efficient absorbing root surface is obtained, thus furnishing the plants with large amounts of water and mineral nutrients.

In humid climates rainfall is relied upon to furnish water to plants. In many cases the annual rainfall is high but most of the precipitation is concentrated at different periods during the year and may not be available when most needed by the crop.

During 1930 the precipitation at New Brunswick was below normal for all months except June. However, the rainfall was rather well distributed throughout the growing season, as shown in figure 1. Therefore, satisfactory yields were obtained in most cases. The rainfall for the growing season of 1931 was only slightly greater.

In the majority of the plots, at the times of observation, the moisture in the surface soil was equal to, or greater than, that of the subsoil. The same condition existed throughout the growing season so far as is known. The rainfall was light and well distributed, and the supposition is that the moisture did not penetrate far into the subsoils except in a few locations. Weaver (41) found that in sub-humid soils root development was stimulated in regions where moisture was concentrated. This may or may not be the case in humid soils. The fact that the surface soil contained as much moisture as the subsoil may be one reason for the failure of the roots to penetrate to deeper horizons. However, it does not explain the reason for limited horizontal root growth in the surface soil. Other factors must be studied in order to explain this.

The pH values of the soils, in general, ranged between 4.5 and 6.0. In practically every case the pH of the subsoil was slightly higher than that of the surface soil. Previous workers have reported that soil acidity increases markedly during the growing season. The tables show that the pH values for the subsoil of the different plots were quite uniform and remained so throughout the season. The surface soil, however, varied considerably, and the values obtained when the plants were mature are slightly higher than those obtained when the plants were young. There are two explanations for this behavior: first, it may be caused by the plants directly, as some investigators propose; second, an increase in acidity may result from the turning under of organic matter, and as this organic matter decomposes the acidity decreases (17). This explanation is borne out in these studies by the fact that the sub-

soil changed very little in pH, while the surface soil, which contained the organic matter, is markedly affected. Also the acidity was less for the second year of testing, and the soil "humus" was greater. Probably both explanations apply to a greater or less extent. At 70 days after planting, when the plants were growing vigorously, the pH of the surface soil was lower than when the plants were mature. This was the case in both 1930 and 1931.

Table 1 shows the average pH and the average soil organic matter of all plots for the four series of observations in the size of seed piece and spacing experiment.

The pH values found are not so low as to interfere with the development of the potato plant. This crop is very tolerant of acid conditions, and this fact is utilized in the control of potato scab (*Actinomyces scabies*).

The organic matter of the soil on the experimental plots was very low, as is characteristic of the soils of this region. There were no significant differences between the various plots. In 1930 the organic matter plowed under did not

TABLE 1

Average soil acidity and percentage of organic matter of potato plots, 1930 and 1931

	1930		1931	
	6/20	7/22	6/25	7/3
Surface soil:				
pH	4.9	5.1	5.0	5.1
Organic matter, *per cent*	1.4	1.3	2.1	2.3
Subsoil:				
pH	5.5	5.6	5.2	5.2
Organic matter, *per cent*	0.5	0.4	1.0	0.9

decompose readily, because of dry weather, so that the percentage of organic matter (humus) was only about half that found in 1931 when more complete decomposition had taken place. The values for the subsoil were about one-third to one-half of those for the surface soil. Organic matter is important in improving the water-holding capacity of the soil, and this may account, in part, for the surface soil having a high moisture content at the time of sampling.

The texture and pore space of the soil are important factors in the development of root systems. Fine-textured soils have greater pore space, but in humid soils more of this pore space will be occupied by water than will that of a coarser textured soil. This factor is important in regions where the rainfall is heavy and soils tend to waterlog. Reduced aeration, in such cases, results in poor plant development. Therefore, it is the custom to improve the aeration of fine-grained soils by increasing the organic matter content.

In these studies most of the soils were either sandy loams or clay loams. The subsoils were generally heavier and in many instances were classed as clays. On drying, these soils tended to become very hard, especially just below

the surface. In several instances the soil was so hard as to prevent the taking of volume weight samples with the sampling tube. It is reasonable, therefore, to suppose that roots would have to overcome considerable resistance in penetrating lower horizons, and since the root system of the potato plant tends to be more or less superficial this resistance might well be sufficient to prevent deep penetration. However, no great penetration was observed even in soils which tended to be sandy.

The pore space of the soils utilized in these studies, in general, varied from 40 to 50 per cent. The pore space of the subsoils was considerably lower. These values are sufficiently high to make aeration a problem in years of high precipitation.

Effects of different fertilizer ratios on potato root development

In 1930 the mature root systems of Irish Cobbler potatoes were investigated in a fertilizer ratio test reported by Martin, Brown, and Sprague (22). Investigations were made on plots receiving the following fertilizer ratios: 0–0–15, 0–15–0, 0–6–9, 9–0–6, 9–6–0, 6–3–6, and 15–0–0.

The general effect of phosphate fertilizers on soils deficient in available phosphorus has been to cause deeper rooting, and, in regions where droughts occur, phosphates are applied to induce shallow-rooted plants to send their roots down to the moist subsoil.

With regard to nitrates the evidence is not quite so clear. Weaver (41) states that where roots come in contact with a soil layer rich in nitrates, they not only develop much more abundantly and branch more profusely but fail to penetrate as far into the deeper soil. On the other hand, Turner (39) claims that nitrates increase the growth of the tops, which in turn require more of the manufactured carbohydrates, thus reducing the carbohydrate supply of the roots and causing less root development. However, it would seem that increased top growth would at the same time provide for an increase in the manufactured plant food. In such case, the roots would not be deprived but would develop more abundantly.

In the fertilizer ratio test investigated in this study, there was apparently little correlation between the fertilizer ratio and the yields and root development.

Table 2 gives the number of main roots per plant, the soil volume occupied by roots, and the yields for the various fertilizer ratios studied. The yields for 1930 were discarded because of heavy infection of spindle tuber in all plots. However, the individual plants studied were apparently normal. The yields given here are the averages for the years 1925–1928. These yields can not be too greatly relied upon since they were observed in other years than those of the root examinations, but they are given in an attempt to explain the results.

The highest yields obtained were from the plots on which the fertilizer ratio 6–3–6 was used. The plants of this treatment had a relatively high number of roots but the soil volume occupied was very low. The lowest yields were

obtained on plots which received the fertilizer ratio 15–0–0. This ratio also gave plants with a low number of roots but the volume occupied was high, thus showing that high concentration of nitrates does not necessarily limit root development. But the supposition is that when a great amount of root and top growth occurs the tubers are not formed and developed as extensively as with other ratios.

According to these data a great number of roots does not necessarily mean a high yield, as shown in the ratio 0–6–9. The high phosphate ratio, 0–15–0, seemed to cause an increase in root development, both in number of roots and branches and extent, but here again the yield was low. The root systems of some of these plots are shown in figure 2.

The conclusions that can be drawn from these data are that extensive root development is not necessarily correlated with high yield and that a fertilizer ratio having medium to large amounts of nitrogen and potassium and a small amount of phosphates gives the highest yields on this soil. The whole problem

TABLE 2

Relation of fertilizer ratio to yield, number of main roots, and volume of soil occupied by roots of potato plants, 1930

FERTILIZER RATIO	NUMBER OF MAIN ROOTS PER PLANT	SOIL OCCUPIED BY ROOTS	YIELD PER A., 1925–1928
		cu. in.	*bu.*
0–15– 0	38	2,660	265
0– 6– 9	50	2,016	255
9– 6– 0	35	2,160	295
6– 3– 6	44	1,260	320
0– 0–15	26	1,200	290
9– 0– 6	36	3,280	315
15– 0– 0	31	3,600	240

needs further investigation before accurate deductions can be made. It is quite probable that the spindle tuber disease affected the root development considerably even though the plants examined appeared to be normal. It is also possible that the fertilizer ratios might markedly affect synthesis and storage of carbohydrates in the tubers without greatly affecting the root system, provided the root system is adequate in all cases.

Effects of size and spacing of seed pieces on potato root development

This experiment was a study of the effects of size and spacing of seed pieces on the yield of Irish Cobbler potatoes and was similar to the one reported by Sprague and Evaul (32). Seed pieces weighing ½ ounce, 1 ounce, and 1½ ounces were spaced at various intervals, and observations of the root systems were made on the various spacings of each of the three sizes of seed pieces. This experiment was conducted in both 1930 and 1931.

During recent years the potato grower of New Jersey has found it to his

advantage to use the smallest sized seed pieces and the widest spacings which will insure optimum development and yield. The most profitable combination is that which will make the most efficient use of the soil and climate at hand. Seed pieces must be large enough to give the plants a good start and the plants should be so spaced that all parts of the soil horizons in which the roots grow will contribute moisture and nutrients to the growing plants.

In brief, the results obtained by Sprague and Evaul (32) were as follows: (*a*) Reducing the space between the seed pieces of the same size increased

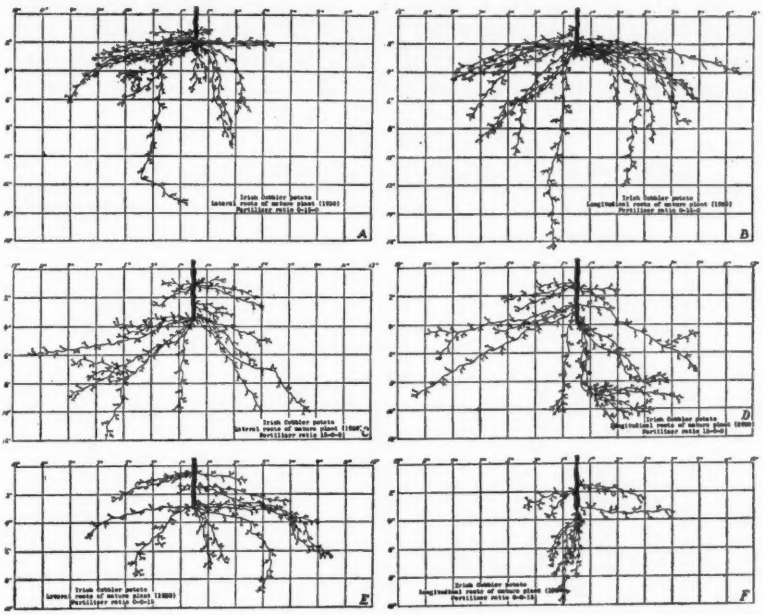


FIG. 2. ONE-HALF OF THE ROOT SYSTEMS OF MATURE IRISH COBBLER POTATO PLANTS OBSERVED IN THE FERTILIZER RATIO TEST, 1930

(A) Lateral roots. (B) Longitudinal roots. Fertilizer ratio 0–15–0.
(C) Lateral roots. (D) Longitudinal roots. Fertilizer ratio 15–0–0.
(E) Lateral roots. (F) Longitudinal roots. Fertilizer ratio 0–0–15.

yields; (*b*) increasing the size of the seed piece greatly increased yields when the spacing in the row remained the same; (*c*) when the total weight of seed used per acre remained constant, the highest yields were obtained from the ½-ounce seed pieces and the lowest from the 1½-ounce pieces; (*d*) when the amount of seed used per acre was subtracted from total yields, the net yields increased with the rate of planting for each size of seed piece; and (*e*) the greatest returns of crop per bushel of seed were obtained from ½-ounce seed pieces spaced at 12 inches in the row.

At the time these tests were carried out it was not clear why the foregoing results were obtained, since no examinations of the root systems were made. Two explanations were offered: (*a*) Closer spacing caused the roots to penetrate deeper into the subsoil, and since a greater soil volume would be occupied the moisture supply of the plant would be greater during the critical periods in July and August; and (*b*) closer spacing may result in a more complete utilization of the fertilizer added.

In these studies the root systems of plants of each treatment were examined 70 days after planting and at maturity. In general, the same relationships existed among yields as those noted in the earlier tests. The yields in 1931 were all lower than expected, however. This was presumably due to the high amount of precipitation in the early part of May, causing an excessive growth

TABLE 3

Effects of size of seed pieces and spacing on the yields of potatoes, 1930–1931

SIZE OF PIECE	SPACING	SEED USED PER ACRE	TOTAL YIELD PER ACRE	YIELD PER BUSHEL OF SEED
oz.	*in.*	*bu.*	*bu.*	*bu.*
½	12	9.1	124	13.6
½	9	12.1	143	11.8
½	7½	14.5	156	10.8
½	6	18.2	171	9.4
1	18	12.1	162	13.4
1	15	14.5	158	10.9
1	12	18.2	185	10.2
1	9	24.2	190	7.9
1½	22½	14.5	139	9.6
1½	18	18.2	154	8.5
1½	13½	24.2	173	7.1
1½	9	36.3	187	5.2

of vines and checking the formation of tubers. Table 3 summarizes the results indicated in the foregoing for the two years 1930 and 1931.

The results agree, for the most part, with those reported by Sprague and Evaul. An examination of the root systems should yield information as to the causes for such results.

Figure 3 represents one-half of the total root system of plants from the various sized seed pieces spaced at 9 inches in the row. The examinations were made 70 days after planting. The most striking fact is the apparent extent of the root systems from different sized seed pieces. The ½-ounce seed pieces show root systems consistently smaller than the larger seed pieces, regardless of the spacing in the row. On the other hand, the root systems of the 1½-ounce seed pieces were consistently larger. The spacing of the plants in the row apparently had little effect on the root systems at this stage. At the

spacing of 9 inches, plants from the ½-, 1-, and 1½-ounce seed pieces had root systems occupying 128, 720, and 2,048 cubic inches respectively. Even if the

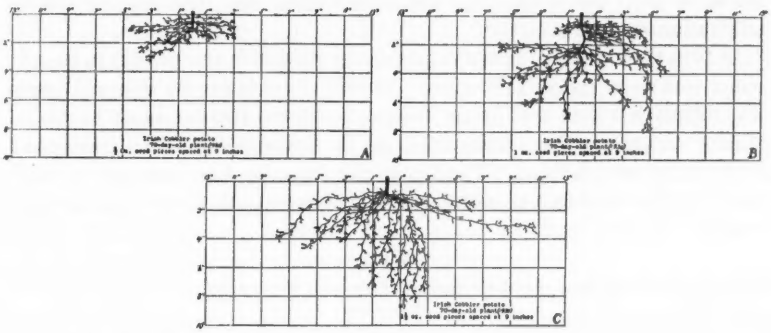


FIG. 3. ONE-HALF OF THE ROOT SYSTEMS OF 70-DAY-OLD IRISH COBBLER POTATO PLANTS GROWN FROM VARIOUS SIZED SEED PIECES AND SPACED AT 9 INCHES IN THE ROW, 1930
(A) ½-oz. seed piece. (B) 1-oz. seed piece. (C) 1½-oz. seed piece.

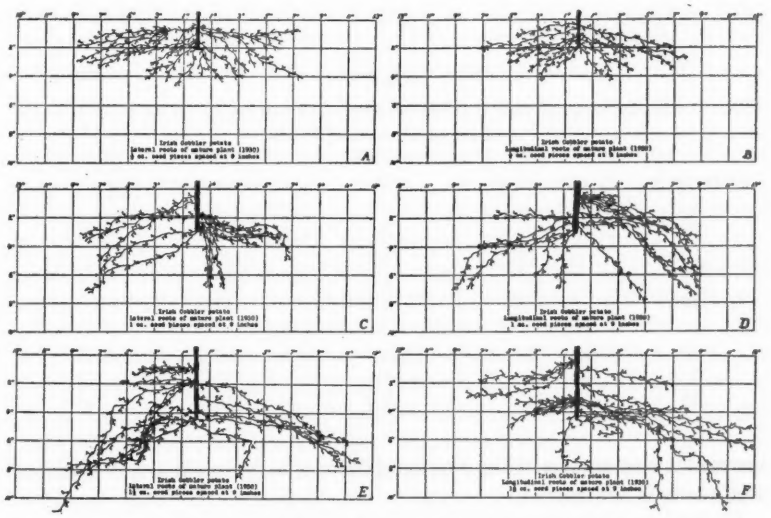


FIG. 4. ROOT SYSTEMS OF MATURE IRISH COBBLER POTATO PLANTS GROWN FROM VARIOUS SIZED SEED PIECES AND SPACED AT 9 INCHES IN THE ROW, 1930
(A) Lateral roots. (B) Longitudinal roots. ½-oz. seed piece.
(C) Lateral roots. (D) Longitudinal roots. 1-oz. seed piece.
(E) Lateral roots. (F) Longitudinal roots. 1½-oz. seed piece.

plants had produced extensive root systems they would hardly have been large enough at this age to make competition a factor.

At maturity the general character of the root systems was about the same. These are shown in figure 4. On the whole, the lateral roots appear to be less extensive than the longitudinal roots, indicating that root pruning during cultivation may be a factor.

In 1930 there was a progressive increase in yield from the ½-ounce to the 1½-ounce seed pieces spaced at 9 inches. In 1931 the yield for the 1½-ounce pieces was slightly less than that for the 1-ounce pieces but this can easily be due to chance variation. The results indicated by Sprague and Evaul correspond with the former condition. The figures given in table 4 are averages for 1930 and 1931, and show that an increase in yield is accompanied by a corresponding

TABLE 4

Effects of size of seed pieces spaced at 9 inches on the yield of potatoes and the soil volume occupied, 1930–1931

SIZE OF SEED PIECE	YIELD PER A.	VOLUME OF SOIL OCCUPIED BY ROOTS OF A SINGLE PLANT
oz.	*bu.*	*cu. ft.*
½	143	25.2
1	190	61.6
1½	187	75.5

TABLE 5

Effects of size of seed piece on yield of potatoes and soil volume occupied when the same amount of seed per acre is used, 1930–1931

SIZE OF SEED PIECE	SPACING IN ROW	SEED PER A.	YIELD PER A.	VOLUME OF SOIL OCCUPIED BY ROOTS IN AN EQUAL AREA
oz.	*in.*	*bu.*	*bu.*	*cu. ft.*
½	7½	14.5	156	107.7
1	15	14.5	158	129.8
1½	22½	14.5	139	77.3
½	6	18.2	166	116.1
1	12	18.2	185	120.9
1½	18	18.2	154	49.5

increase in root volume, if the 3-bushel difference between the 1- and 1½-ounce seed pieces is disregarded.

If the plots in which the same amount of seed per acre is used are compared, the figures shown in table 5 are obtained.

The root volume of a single plant was multiplied by 3 in the case of the ½-ounce seed piece and by 2 in the case of the 1-ounce seed piece in order to bring the number of plants per unit area to a common basis.

The figures show that the yield from the 1-ounce pieces is greater than that from the ½-ounce pieces and also that the root volume increases. Furthermore, the yield from the 1½-ounce pieces is below that from the ½-ounce pieces, and

the same is true of the soil volume occupied. Hence, it may be concluded that the plants produced by 1-ounce seed pieces utilize the soil more efficiently than do those produced by the ½-ounce or 1½-ounce pieces. Table 3 shows that the greatest yield per bushel of seed used is produced by the ½-ounce seed pieces spaced at 12 inches. This also must be due to the more efficient use of the fertilizer and soil moisture.

It is a common practice in this region to apply large amounts of fertilizers to a potato crop. This has given good results as far as the potatoes are concerned, but there is a certainty that all the fertilizer is not utilized by the plants. Several investigators have reported that the residual effects on the following crops are quite marked. This indicates that less fertilizer is required as the plants are spaced farther apart in the row.

The evidence in these studies seems to show that the large amounts of fertilizers applied to the surface soil, where moisture is usually plentiful, tend to produce limited root systems both in the horizontal and the vertical directions. There is need for information on the effects of fertilizers applied to the lower soil horizons. As long as soil moisture is sufficient in the surface soil an extensive root system is not required where large amounts of fertilizers are used, but in times of drought a plant with a deep-seated root system has a decided advantage over one with a superficial system. It may be that in these soils deeper applications of fertilizers would result in deeper root systems.

Effects of soil conditions on root development of red clover

The clover plants utilized in these studies were a part of a strain test of red clover. The results of a previous test of this nature are given by Sprague, Evaul, Reuszer, and Farris (33). Strains from Ohio, Michigan, and France were studied, both spring and fall seedings being used.

Most investigators have reported that red clover possesses a tap root which penetrates very deeply. Also an extensive system of laterals is usually present. The deeply penetrating character is associated with a deep, mellow soil which is well drained. The roots do not penetrate far into heavy, wet soil. The early work of Hays (24) in Minnesota showed that red clover, in addition to being deeply penetrating, also possessed a great number of laterals, in many cases penetrating as far as, or farther than, the tap root itself.

Weaver (41) found that root development in the second year of growth consisted mainly in deeper penetration and growth of a few additional laterals. In other words, the territory later to be fully occupied by the roots is blocked out early in their growth.

In New York (24), on a heavy clay soil, the tap roots of red clover reached a depth of 34 inches the first season, and branches occurred throughout their length, with some of the branches extending 12 inches from the tap root.

In the present study the root systems of the clover plants observed tended to be shallower than would be expected from previous reports on the root development of this plant. In general, growth during the first year was limited to

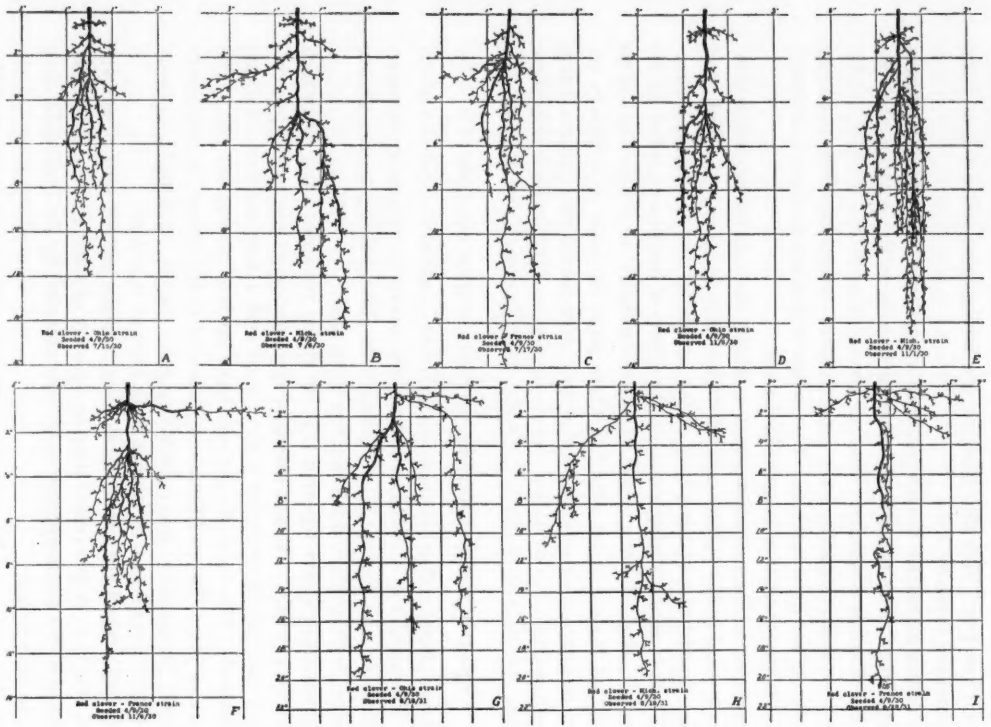


FIG. 5. ONE-HALF OF THE ROOT SYSTEMS OF DIFFERENT STRAINS OF RED CLOVER SEEDED APRIL 9, 1930

(A) Ohio; 3 months old. (B) Michigan; 3 months old. (C) France; 3 months old.
(D) Ohio; 7 months old. (E) Michigan; 7 months old. (F) France; 7 months old.
(G) Ohio; 16 months old. (H) Michigan; 16 months old. (I) France; 16 months old.

about 3 inches in the horizontal direction and 14 inches in depth. This is a decided contrast to the observations of Weaver in Nebraska, where he found roots of 1-year-old plants penetrating to a depth of 4 and 5 feet and branches extending to 8 or 12 inches in the horizontal direction before turning downward. Evidence from these studies seems to indicate that the amount of soil moisture at the time of seeding is an important factor in the later development of the root system.

Figures 5 and 6 represent one-half of the root systems of the plants studied during 1930 and 1931.

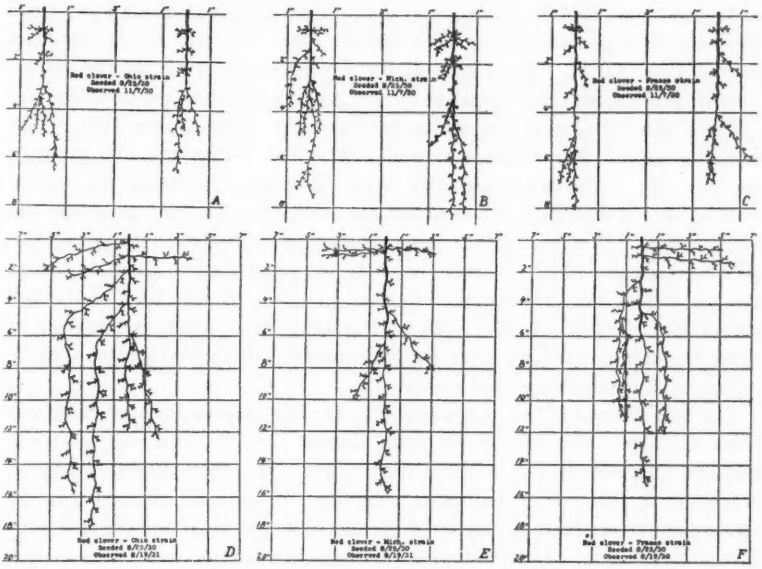


FIG. 6. ONE-HALF OF THE ROOT SYSTEMS OF VARIOUS STRAINS OF RED CLOVER SEEDED AUGUST 25, 1930

(A) Ohio; 2½ months old. (B) Michigan; 2½ months old. (C) France; 2½ months old.
(D) Ohio; 12 months old. (E) Michigan; 12 months old. (F) France; 12 months old.

At the time of the spring seeding, April 9, 1930, the soil was very dry, and little precipitation occurred until the middle of June, as is shown in figure 1. This slowed up germination of the seed and undoubtedly had a marked effect upon the formation of the root systems.

The first observations were made about June 13, 1930, when the plants were about 35 days old. Since about an inch of rain fell just prior to this examination, the soil was in good condition as regards moisture. The moisture content of the soil at this time was about 20 per cent and that of the subsoil about 22 per cent. It was evident that the branching was much more extensive than is

usual with plants of this age. The French strain was especially greatly branched. The depth of penetration was only about 7 inches.

At the second observation, July 15, 1930, the moisture content of the soil was only about half that at the previous examination. The root systems shown in figure 5 still indicate a noticeable modification of the tap root system. It was difficult, in most cases, to determine which was the tap root below a depth of 4 inches. The roots had extended to a depth of 12 to 14 inches at this time, and the branches extended laterally about 2 inches.

The last observation of the spring seeding in 1930 was made about November 5, the plants being about 7 months old at this time. The moisture of the surface soil was about 15 per cent and that of the subsoil was about 9 per cent. The roots had penetrated but little farther than they had at the previous examination (fig. 5). The plants of the French strain were, on the whole, more shallow rooted than the native strains, and branching was more extensive.

Three observations of the spring seeding were made during 1931. The moisture supply was ample and well distributed throughout the growing season. The roots had apparently made little growth during the winter months, as the distribution was about the same May 15, 1931 as it was the previous fall. However, rather rapid development occurred throughout the growing season of 1931. In July the roots had penetrated to about 17 inches and the lateral branches extended to over 5 inches. At the time of the last observation, August 18, 1931, the root systems were about as pictured in figure 5. In most cases, however, the French strain still showed greater branching and a more superficial root system.

The root systems of the plants seeded in the fall presented entirely different characteristics. The seeding was made August 25, 1930, at a time when the moisture content of the soil was very high. The observations made on November 7, 1930, when the plants were about 75 days old, showed that the root systems were more distinctly of the tap root type than was the case with the spring seeding. Little difference between the strains was noted at this time. Figure 6 illustrates the root systems at this observation.

More extensive root growth took place during the winter months than was the case with the plants of the spring seeding. The depth of penetration increased about 3 inches and the lateral spread about 2 inches. It is possible that the plants grew more vigorously in the early spring than did those of the spring seeding.

In July the tap roots had penetrated to a depth of about 14 inches and the lateral branches had reached about 4 inches.

By the latter part of August the tap roots had reached about 16 inches in depth, which is a greater depth than for the spring seeding plants of the same age. Here again, the strain from France had a more branched and superficial root system.

The pH of the soil was fairly uniform throughout the experiment. The average pH of the surface soil was 6.1 during the first year and decreased to 5.9

for the second year. The acidity of the subsoil was practically constant. The lower value for 1931 is undoubtedly due to the utilization of lime by the plants. Since the red clover plant is very intolerant of acid conditions it is possible that better growth would have occurred if the soil acidity had been less.

The organic matter content of the soil was slightly higher the second year, especially in the surface soil, the values for 1930 being 1.6 per cent for the surface soil and 0.9 per cent for the subsoil. In 1931 the organic matter content of the surface soil was 2.1 per cent and that of the subsoil 1.2 per cent. The amount of organic matter was so uniform throughout the plots that any differences occurring between the various strains can not be attributed to this soil factor.

The determinations for phosphorus, nitrogen, and potassium indicate that by far the greatest amounts of available nutrients, especially phosphorus, are concentrated in the plow zone. Evidently there is little loss of nutrients by leaching in this soil.

The soil which was utilized for these plots is a little heavier than that on which the potatoes were grown. Most of the surface soil is classed as a clay loam while the subsoil is a sandy clay or clay. The pore space of the surface soil averaged about 48 per cent and that of the subsoil a little lower. The subsoil is very heavy and hard when dry, and roots would have to overcome considerable resistance in penetrating it in that condition.

The number of branch roots did not appear to increase during the second year of growth. The volumes of soil occupied by roots are much greater the second year, largely because of the deeper penetration of the tap roots and their branches.

An additional observation was made of native red clover in the fall of 1931 and the spring of 1932. The clover was seeded in the spring of 1931 on a light sandy loam soil underlaid by light sandy loam subsoil. In November the plants had well-developed tap roots penetrating to depth of about 30 inches. The laterals had reached a distance of about 5 inches from the tap root. In April 1932, the tap roots had reached a depth of about 36 inches. Evidently the favorable moisture conditions and light soil had materially aided the development of a good tap root system on this field.

Effects of soil conditions on the root development of corn

The corn plant has a coarse fibrous root system which spreads widely and penetrates deeply, according to several investigators. Most observations have been made on deep, mellow, fertile soil where one would naturally expect root systems to attain a maximum development. Like the other cereals the first whorl of roots arises within an inch or two of the surface of the soil, even if the seed is planted several inches deep. All the roots arise from the nodes of the stem in whorls and it is not uncommon to find roots arising from the first

one or two nodes above the surface of the soil. However, these roots do not branch until they reach the soil.

In these studies the root systems of several corn varieties were examined on different soil types in both 1930 and 1931. These observations included both checked and drilled corn. In 1931, root examinations were made in a test of different methods of corn cultivation.

Weaver (41) made observations of corn grown on loess soil in eastern Nebraska when the plants were 36 days old. At this time the roots extended laterally to 2.5 feet and were confined largely to the first foot of soil. In the present studies 44-day-old corn plants of the Mercer White Cap variety, grown on a fairly light sandy loam soil, were examined June 26, 1930. These plants were spaced 40 inches apart each way. Figure 7 (A) represents the

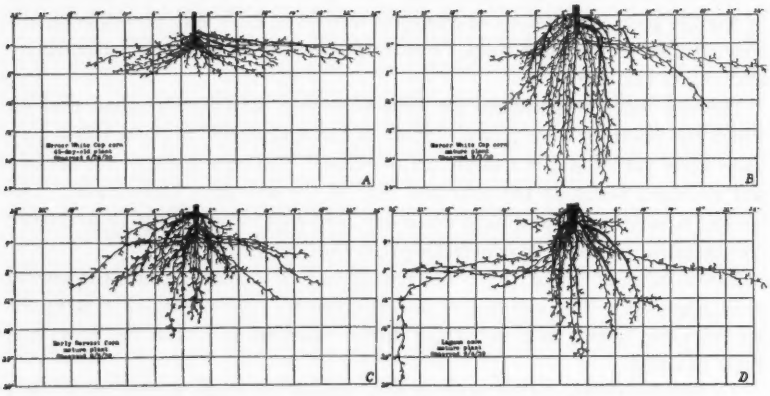


FIG. 7. ONE-HALF OF THE ROOT SYSTEMS OF THREE VARIETIES OF CORN, 1930
(A) Mercer White Cap; 45-day-old plant. (B) Mercer White Cap; mature plant.
(C) Early Harvest; mature plant. (D) Laguna; mature plant.

appearance of the plant roots at this time. Most of the roots extended laterally to 16 or 18 inches and very few had penetrated beyond a depth of 8 inches.

A mature root system of a plant grown on the same soil is shown in figure 7 (B). The most striking fact is the short extension of the lateral roots. There was evidence of considerable root pruning from cultivation, which accounts for this appearance. The depth of penetration seemed to be about 24 inches. Many of the brace roots formed at or above the soil surface were among the most deeply penetrating ones.

The soil moisture content was low at the time of observation, September 3, 1930, but figure 1 shows that the moisture was distributed throughout the growing season so that, in all probability, normal growth took place.

The root systems shown in figure 7 (C and D) are those of two different varieties of corn. C is a variety known as Early Harvest, which has been

developed by D. H. Rising of Easton, Pa. This variety should be well adapted to this region. The root system of this variety was much less extensive than that of the Mercer White Cap. The maximum spread was 18 inches, and the greatest depth was about 16 inches. D is the Laguna variety. The seed of this variety came from Mississippi. The top growth was exceedingly tall and rank. The roots showed evidence of extensive pruning in the upper few inches of soil but several roots extended horizontally as far as 28 inches and vertically to a depth of 24 inches.

These studies indicate that various varieties of corn may differ widely in their root systems. It is also entirely possible that even different plants of the

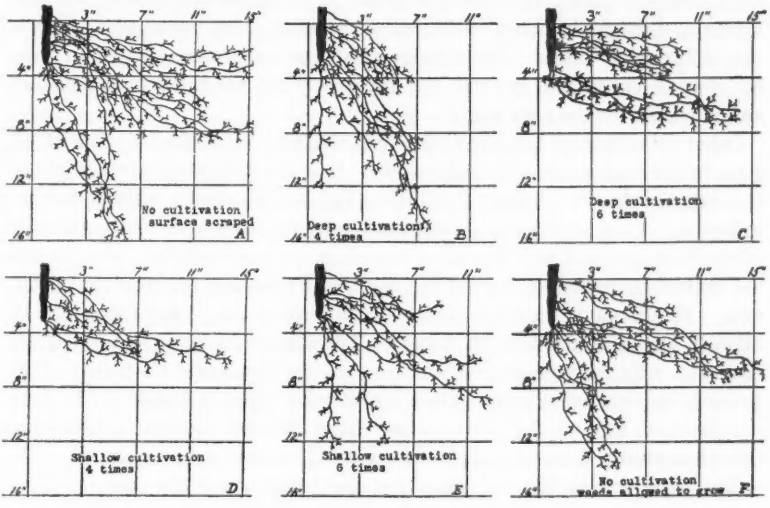


FIG. 8. ONE-FOURTH OF THE MATURE ROOT SYSTEMS OF LANCASTER SURE CROP CORN UNDER DIFFERENT METHODS OF CULTIVATION, 1931

(A) No cultivation, surface scraped. (B) Deep cultivation four times.
(C) Deep cultivation six times. (D) Shallow cultivation four times.
(E) Shallow cultivation six times. (F) No cultivation, weeds let grow.

same variety will show great differences in their root systems, since corn varieties are not homozygous. It would be interesting to study the root systems of selfed lines of corn in addition to single and double crosses between the lines.

In 1931 a cultivation experiment was conducted with Lancaster Sure Crop corn. The soil utilized for this experiment had had 3 or 4 inches of the surface soil removed several years previously and it had been seeded to timothy for 3 or 4 years previous to this experiment, so that a fairly heavy sod was plowed under. The surface soil was classed as a clay or clay loam and the subsoil as a sandy loam. The plants were spaced at 40 inches each way and the plots cultivated in both directions.

Figure 8 illustrates the root systems found in these observations.

The highest yields were obtained from the plots receiving deep cultivation six times and the next highest from plots which were cultivated shallow six times. However, these yields were only slightly greater than the ones obtained from the plots which received no cultivation, the weeds being kept down by scraping with a hoe. Shallow cultivation and deep cultivation four times were apparently not as effective as the greater number of cultivations. The yields of the plots in which the weeds were allowed to grow were, of course, decidedly inferior.

An examination of the root systems showed that in the plots receiving no cultivation, the weeds being kept down by hoeing, the root systems were much more extensive than in the cultivated plots. The volume occupied by the root system is 9,464 cubic inches, while that of the plots giving the highest yields is only 3,388 cubic inches. The plots in which the weeds were allowed to grow had very extensive root systems, but apparently the weeds left little moisture and nutrients for the corn plants.

Other investigators have reported that shallow cultivation or none at all gives better results than deep cultivation (12). The differences are so slight in this experiment that definite conclusions can not be drawn without further evidence. A suggestion may be proposed, however, that where large amounts of fertilizer are used and rainfall is abundant the root systems, even though not extensive, are able to supply the plant with adequate moisture and nutrients. Furthermore, on heavy soil, root pruning by deep cultivation may be offset by loosening and aerating the soil. The plants may be able to regenerate roots at a sufficiently rapid rate to insure good development of the plant. This problem requires more investigation on different types of humid soils. It is reasonable to suppose that humid soils require different cultivation, as well as other treatments, from the soils in the sub-humid or semi-arid regions.

The other soil factors and plant responses were about the same as those discussed for potatoes and clover in the previous sections.

GENERAL DISCUSSION

One conclusion that can be drawn from these studies is that the root systems of many crop plants are decidedly different on the humid soils of New Jersey from those reported by workers in other regions. The general forms of the root systems may be similar but they are much less extensive than those observed in the lighter and drier soils of the western and mid-western states. Weaver reports observations of potatoes in which the roots extended laterally more than 2 feet and penetrated to a depth of more than 4 feet. In this study very few roots extended laterally more than 1 foot and the vertical depth to which they penetrated was seldom more than 10 to 12 inches. Reports have been made of mature red clover in which the tap roots penetrated to depths of more than 8 and 10 feet, but observations in this locality failed to discover roots which penetrated farther than 3 feet, and lateral branching was also noticeably limited. Other workers have observed corn roots which had a lateral spread of

over 4 feet and a vertical extent of 8 feet and more, whereas the corn roots in this soil were limited to the first 2 feet of soil and extended laterally not more than 2 feet.

In general, the number of roots per plant and the amount of branching of the main roots, in each crop studied, seemed to be less than those observed by other investigators in other soil groups.

The different soil factors must be held accountable for these differences, since the roots are very little affected by conditions above their immediate environment. It is usually the roots which influence the above-ground parts of the plants.

The soil reaction is ordinarily corrected by liming to suit the requirements of a particular crop, and this factor does not seem to be very influential in modifying the root system as long as the plant as a whole makes the optimum development.

The main influence of soil organic matter on fertilized soils is to increase the water-holding capacity of the soil and to improve the structure of heavy, fine-textured soils. In the soils on which these tests were conducted very little organic matter was found below the plow zone. Even in soils where roots penetrate to great depths, little organic matter is present in the lower horizons. Apparently then, this factor influences root development very little on these soils. If it were very influential the lateral spread of roots in the surface soil should be greater than has been observed.

The pore space found in these soils is estimated to be adequate except during a period when high precipitation occurs. Some soils of this region are not well drained, and pore space may then be a factor influencing normal root development.

The soil texture itself should not be a very important factor in root development as long as moisture and nutrients are adequate. Roots have been found to penetrate deeply into heavy clay subsoils and even through hardpans, but this probably occurs when these layers are moist and soft.

It is believed that the factors which most influence root development in the humid soils are moisture and mineral nutrients. Since the rainfall is usually ample in this region, the surface soil contains a fair amount of moisture at all times. Even after several days of dry weather the surface soil may contain as much moisture as the subsoil. Thus the necessary stimulus is not provided to cause plants to penetrate deeply into the soil for moisture. In the case of clover it is suggested that the moisture content of the soil at the time of germination and early seedling growth has a great influence on the formation of the root system. Plants which start in a relatively dry soil seem to have shallower and more branched root systems, even at maturity, than those plants which start their growth with an adequate supply of soil water.

Coupled with the moisture supply is the supply of available nutrients. Large amounts of commercial fertilizers are used on the soils of this region and from determinations made in this study most of the available nutrients are

concentrated in the surface soil or plow zone. Apparently very little is carried down into the lower horizons. Thus it seems natural to assume that the growth of plant roots would be restricted by chemotropism to those soil layers in which the most available nutrients occur. Also where very large amounts of fertilizer are used, as with potatoes, the root growth would likewise be restricted in a horizontal direction. Hence, plants can be spaced closer together in order to utilize more of the soil, or the fertilizer rate can be reduced for the wider spacings.

Several additional problems have presented themselves during these investigations. In the first place no studies were made of the influences of soil organisms on root growth. It is almost certain that the action of micro-organisms may have considerable influence on root development, probably largely through the composition of the soil air and organic matter changes.

Further work should be done on the effects of different types of cultivation. The evidence in this experiment is not decisive enough to warrant definite conclusions. It may be that on these soils the weed factor is not the only one which makes cultivation necessary.

The results of these studies indicate a need for more knowledge concerning the application of fertilizers. In other localities the subsurface application of fertilizers has proved beneficial by causing the plants to root deeper into the soil. This is especially important if the surface soils tend to dry out readily.

Finally, observations of corn root systems indicate that there is a wide diversity among the different varieties. Even within one variety the root systems of individual plants may be quite different. Hence, a study of the root systems of selfed lines of corn should be very beneficial in producing superior strains.

SUMMARY

Observations of the root systems of white potatoes, red clover, and corn were made during 1930 and 1931 with the purpose of determining the relations between the various soil characteristics and root development.

The root systems of all the plants studied were very much less extensive than those reported in the sub-humid and semi-arid regions of the western and mid-western states. Potato roots were limited to the first foot of soil, and lateral extent was seldom greater than 1 foot. The root systems of red clover did not penetrate farther than 3 feet even under the most favorable conditions. Corn roots extended no farther than 2 feet either laterally or vertically.

The soil acidity, per cent of organic matter, pore space, and soil texture apparently have little influence on root extension, although the pore space may be important in seasons of high rainfall.

The evidence indicates that the amount of soil moisture, at the time of seeding, influences the form of clover root systems to a large degree. Also the ample rainfall in this region seems to give plant roots very little stimulus to penetrate to the lower soil layers.

Coupled with the influence of soil moisture is the supply of mineral nutrients. Large amounts of commercial fertilizers are used in this region and most of this fertilizer is concentrated in the surface soil. Therefore plants are not provided with the necessary stimulus to develop extensive root systems.

The higher yields of white potatoes from small seed pieces spaced close together are apparently due to the more extensive utilization of the soil by the plant roots.

Different fertilizer ratios apparently had little effect on potato root systems. Differences were noted in the yields but this may be due to the direct influence of the fertilizer on the translocation of food to the tubers.

Various varieties of corn present quite different root systems. In general, the plants with the largest top growth had the most extensive root systems.

The differences in yields and root development of corn receiving different types of cultivation were very slight, and the evidence obtained is not conclusive enough to warrant recommendations. It is possible that the weed factor may not be the only one which makes cultivation necessary.

Additional problems suggested for investigation are: (*a*) the influence of micro-organisms on root development; (*b*) further studies on methods of cultivation; (*c*) the influence of the depth of fertilizer application on root development; and (*d*) studies of the root systems of selfed lines of corn and hybrids of these lines.

REFERENCES

(1) Bose, R. D., and Dixit, P. D. 1931 Studies in Indian barleys: II. The root system. *Indian Jour. Agr. Sci.* 1: 58–59 (Abst. in *Exp. Sta. Rec.* 66: 326).

(2) Bouyoucos, G. J. 1930 A comparison of the hydrometer method and the pipette method for making mechanical analysis of soils, with new directions. *Jour. Amer. Soc. Agron.* 22: 747–751.

(3) Bray, R. H. 1932 A test for replaceable and water-soluble potassium in soils. *Jour. Amer. Soc. Agron.* 24: 312–316.

(4) Brown, B. A. 1924 Spacing of potato hills. *Storrs Agr. Exp. Sta. Bul.* 119.

(5) Bryan, O. C. 1923 Effect of reaction on growth, nodule formation and calcium content of alfalfa, alsike clover and red clover. *Soil Sci.* 15: 23–35.

(6) Cannon, W. A. 1912 Physical relations of roots to soil factors. *Carnegie Inst. Wash. Yearbook* 11: 61–62.

(7) Cannon, W. A. 1918 Modification of root habits by experimental means. *Carnegie Inst. Wash. Yearbook* 17: 83–85.

(8) Cannon, W. A. 1921 Root growth in relation to a deficiency of oxygen or an excess of carbon dioxide in the soil. *Carnegie Inst. Wash. Yearbook* 20: 48–51.

(9) Cannon, W. A. 1924–25 Experimental studies on roots. *Carnegie Inst. Wash. Yearbook* 24: 289–298.

(10) Cannon, W. A. 1925–26 Studies on roots. *Carnegie Inst. Wash. Yearbook* 25: 317–325.

(11) Cannon, W. A. 1932 On the variation of the oxygen content of cultural solutions. *Science* 75: 108–109.

(12) Cates, J. S., and Cox, H. R. 1912 The weed factor in the cultivation of corn. U. S. Dept. Agr. Bur. Plant Indus. Bul. 257.

(13) Degtjareff, W. T. 1930 Determining soil organic matter by means of hydrogen peroxide and chromic acid. *Soil Sci.* 29: 239–245.

(14) EAMES, A. J., AND MACDANIELS, L. H. 1925 An Introduction to Plant Anatomy. McGraw-Hill, New York.

(15) GEORGESON, C. C., BURTIS, F. C., AND OTIS, D. H. 1897 Experiments with corn. Kans. Agr. Exp. Sta. Bul. 64.

(16) HENDRICKSON, A. H., AND VEIHMEYER, F. J. 1931 Influence of dry soil on root extension. *Plant Physiol.*, 6: 567–576.

(17) HILL, H. H. 1919 A comparison of methods for determining soil acidity and a study of the effects of green manures on soil acidity. Va. Agr. Exp. Sta. Tech. Bul. 19.

(18) HUTCHESON, T. B., HODGSON, E. R., AND WOLFE, T. K. 1917 Corn culture. Va. Agr. Exp. Sta. Bul. 214.

(19) LEBEDEV, A. F. 1928 The volume weight of soils as a physical characteristic of the soil profile. *Soil Sci.* 25: 207–211.

(20) LYON, T. L., AND BUCKMAN, H. O. 1926 The Nature and Properties of Soils. MacMillan, New York.

(21) LYON, T. L., AND WILSON, J. K. 1921 Liberation of organic matter by roots of growing plants. N. Y. (Cornell) Agr. Exp. Sta. Mem. 40.

(22) MARTIN, W. H., BROWN, B. E., AND SPRAGUE, H. B. 1931 The influence of nitrogen, phosphoric acid and potash on the number, shape and weight of potato tubers. *Jour. Agr. Res.* 43: 231–260.

(23) MILLAR, C. E. 1925 Availability of nutrients in subsoils. *Soil Sci.* 19: 275–285.

(24) MILLER, E. C. 1916 The root systems of agricultural plants. *Jour. Amer. Soc. Agron.* 8: 129–154.

(25) MORGAN, M. F. 1930 A simple spot plate test for nitrate nitrogen in soil and other extracts. *Science* 71: 343–344.

(26) MORROW, G. E., AND HUNT, T. F. Field experiments with corn. *Ill. Agr. Exp. Sta. Bul.* 4: 113–115 (1889); 8: 263–266 (1890).

(27) PARTRIDGE, N. L., AND VEATCH, J. O. 1932 The relationship between soil profile and root development of fruit trees. *Mich. Agr. Exp. Sta. Quart. Bul.* 14: 200–207.

(28) SCHREINER, O., AND SKINNER, J. J. 1918 The triangle system for fertilizer experiments. *Jour. Amer. Soc. Agron.* 10: 225–249.

(29) SEWELL, M. C. 1919 Tillage: A review of the literature. *Jour. Amer. Soc. Agron.* 11: 269–290.

(30) SMITH, A. M., AND ROBERTSON, I. M. 1931 The influence of the plant upon seasonal changes in soil acidity. *Jour. Agr. Sci.* 21: 822–831.

(31) SMITH L. H., AND WALWORTH, E. H. 1926 Seminal root development in corn in relation to vigor of early growth and yield of crop. *Jour. Amer. Soc. Agron.* 18: 1113–1120.

(32) SPRAGUE, H. B., AND EVAUL, E. E. 1929 Effect of size of seed piece and rate of planting on yields of white potatoes. *Jour. Amer. Soc. Agron.*, 21: 513–523.

(33) SPRAGUE, H. B., EVAUL, E. E., REUSZER, H. W., AND FARRIS, N. F. 1930 Experiments with alfalfa, clover and timothy for hay in New Jersey. N. J. Agr. Exp. Sta. Bul. 512.

(34) SPRAGUE, H. B., AND FARRIS, N. F. 1931 The effect of uniformity of spacing seed on the development and yield of barley. *Jour. Amer. Soc. Agron.* 23: 516–533.

(35) THOMAS, M. D. 1928 Soil structure as influenced by mechanical treatments and soluble salts. *Soil Sci.* 25: 409–418.

(36) THOMPSON, H. C. 1921 Effects of cultivation on soil moisture and on yields of certain vegetables. *Proc. Amer. Soc. Hort. Sci.* 1920: 155–161.

(37) TRUOG, E. 1916 The utilization of phosphates by agricultural crops. Wis. Agr. Exp. Sta. Res. Bul. 41.

(38) TRUOG, E. 1930 The determination of the readily available phosphorus of soils. *Jour. Amer. Soc. Agron.* 22: 874–882.

(39) TURNER, T. W. 1922 Studies of the mechanisms of the physiological effects of certain mineral salts in altering the ratio of top growth to root growth in seed plants. *Amer. Jour. Bot.* 9: 415–445.
(40) WAKSMAN, S. A. 1927 Principals of Soil Microbiology. Williams & Wilkins, Baltimore.
(41) WEAVER, J. E. 1926 Root Development of Field Crops. McGraw-Hill, New York.
(42) WEAVER, J. E., AND BRUNER, W. E. 1927 Root Development of Vegetable Crops. McGraw-Hill, New York.
(43) WOLFANGER, L. A. 1930 The Major Soil Divisions of the United States. Wiley and Sons, New York.

APPLICATION OF THE THEORY OF PROBABILITY TO THE SIZE DISTRIBUTION OF SOIL AGGREGATES[1]

CLARK AFFLECK[2]

Utah Agricultural Experiment Station

Received for publication September 5, 1933

In the study of mechanical analysis of soils extreme care is taken to obtain size-distribution curves of the various soils. These curves give a real picture of how the soils are made up mechanically. A crude example of a size-distribution curve may be described somewhat as follows:

Suppose a large number of small boxes of uniform width are placed side by side to form a long row, numbered from left to right with consecutive integers 1, 2, 3, 4, etc. Imagine a soil or some other finely divided substance graded according to size of particle, and the extremely small particles placed in the first box, those larger in radius by a small definite amount placed in the second, and so on, until extremely large particles are placed in the last box to the right. Let a vertical line be erected from the center of each box with a length proportional to the weight of material within the box from which it is drawn, and a smooth curve drawn through the end points of all the lines. It is natural to expect a humpbacked curve or one that touches the axis of abscissas where it has small and large values, and has one or more maxima at intermediate points. This actually has been found to be the case with soils.

An interesting problem arises: What is the most probable distribution when a given amount of some homogeneous substance is broken into fine particles by a random process? To attempt an answer to this question it will be necessary to make use of the theory of probability to develop an algebraic expression for the distribution. The particles will be classified in the order of increasing radius and will be identified with the various intervals which are one unit wide.[3]

If N is the total number of particles and N_r the number of particles identified with any particular radius interval corresponding to the discontinuous variable r, which is the average radius of the particles within an interval r_a to r_b,

$$\Sigma N_r = N. \qquad (A)$$

The fractional number of all the particles that are associated with any one radius interval may be defined by the equation

[1] Contribution, physics department, Utah Agricultural Experiment Station. Publication authorized by director, August 30, 1933.

[2] Graduate student.

[3] The following discussion to and including equation (*R*) is taken essentially from Arthur Haas' "Introduction to Theoretical Physics," vol. 2.

$$w_r = \frac{N_r}{N} \tag{B}$$

It must follow that

$$\Sigma w_r = 1. \tag{C}$$

Written in the general form the statistical probability of a distribution is expressed by the equation

$$W = \frac{N!}{N_1!\, N_2! \cdots N_r! \cdots} \tag{D}$$

where $N_1, N_2, \ldots N_r, \ldots$ are the numbers of particles contained in the respective radius intervals, characterized by the subscripts. This expression can be greatly simplified and made more accessible to calculation by writing it in the logarithmic form, by the use of Stirling's formula, which is:

$$\log_e (n!) = n \log_e n - n + 1/2 \log_e (2\pi n).$$

For large values of n the last term is obviously small compared with the others, and the equation may be written

$$\log_e (n!) = n \log_e n - n. \tag{E}$$

Taking the logarithm of (D) and using (E),

$$\log_e W = N \log_e N - N - \Sigma N_r \log_e N_r + \Sigma N_r.$$

Using (A) and (B),

$$\log_e W = N \log_e N - \Sigma N w_r (\log_e N + \log_e w_r),$$

or

$$\log_e W = N \log_e N - N \log_e N \Sigma w_r - N \Sigma w_r \log_e w_r.$$

Finally by using (C)

$$\log_e W = - N \Sigma w_r \log_e w_r. \tag{F}$$

A given volume V of material is to be broken into a given number of particles N and distributed in such a way that the statistical probability W has a maximum value. These conditions may be stated mathematically by:

$$\delta W = 0, \quad \text{or} \quad \delta(\log_e W) = 0. \tag{G}$$

$$\delta N = 0. \tag{H}$$

$$\delta V = 0. \tag{I}$$

In accordance with (B) and (C), the constancy of the total number of particles may be written

$$\Sigma \delta w_r = 0. \tag{J}$$

If V_r is the volume of a single particle whose radius is characterized by the index r,

$$V = \Sigma N_r V_r \tag{K}$$

and

$$\delta V = \Sigma V_r \delta N_r. \tag{L}$$

By (I) the left-hand side of (L) is zero. Using (B), (L) may be rewritten

$$\Sigma V_r \delta w_r = 0. \tag{M}$$

This expresses the constancy of the total volume V.

By taking the variation of (F).

$$\delta(\log_e W) = - N\Sigma \log_e w_r \delta w_r - N \Sigma\delta w_r. \qquad (N)$$

The left-hand side is zero by (G) and the last term vanishes by (J); and since N cannot be zero the constancy of the probability may be written

$$\Sigma \log_e w_r \delta w_r = 0. \qquad (O)$$

In order to obtain a solution for w_r that will satisfy the three equations (J), (M), and (O), undetermined constants will be multiplied by each of equations (J) and (M) and the equations then added to equation (O), thus

$$\Sigma(\log_e w_r + \lambda_1 V_r + \lambda_2)\delta w_r = 0 \qquad (P)$$

where equation (M) is multiplied by λ_1 and (J) by λ_2. As the variation δw_r in general is arbitrary the equation can be satisfied only when the quantity in the brackets vanishes, thus

$$\log_e w_r = - \lambda_2 - \lambda_1 V_r$$

or

$$w_r = e^{-(\lambda_2 + \lambda_1 V_r)}. \qquad (Q)$$

Introducing two new factors $\lambda_1 = 1/\theta$ and $\lambda_2 = \psi/\theta$ (Q) becomes[4]

$$w_r = e^{(\psi - V_r)/\theta}. \qquad (R)$$

Substituting the value for w_r from (B)

$$N_r = NCe^{-(V_r/\theta)}. \qquad (S)$$

where $C = e^{\psi/\theta}$. Now $V_r = 4/3\ \pi r^3$ giving

$$N_r = NCe^{-(4/3\pi r^3)/\theta}. \qquad (T)$$

Multiplying both members by $4/3\ \pi r^3\rho$ where ρ equals the density of the material used,

$$4/3\pi\ r^3\rho N_r = NC\ (4/3\pi r^3\rho)\ e^{-4/3\pi r^3)/\theta}. \qquad (U)$$

The quantity on the left is the mass of the material in the radius interval corresponding to r which will be denoted by q_r. The quantity on the right can be simplified by introducing two more constants $A = 4/3\ \pi\rho NC$ and $E = e^{-(4/3\pi)/\theta}$.

Thus (U) becomes

$$q_r = Ar^3E^{-r^3}. \qquad (V)$$

In this equation r is a discontinuous variable having only integral values. If this expression is plotted in histogram fashion and a smooth curve passed through the points (r, q_r) the subscript may now be dropped and the continuous function

$$q = Ar^3E^{-r^3}. \qquad (W)$$

will approach the histogram in form as the radius intervals become extremely small.

The constant θ is as yet undetermined. By taking the derivative of (W) with respect to r and equating it to zero it is found that $[1 - r^3 \log_e E]$ must equal zero at the curve maximum or

$$r^3 = 1/\log_e e^{(4/3\pi)/\theta} = \theta/(4/3\pi). \qquad (X)$$

$$\theta = 4/3\ \pi\ r_m^3.$$

[4] The distribution that corresponds to this equation is known as "Gibbs' canonical ensemble."

Where r_m is defined as the value of r where the curve has its maximum ordinate q. Thus,

$$E = e^{(4/3r)/0} = e^{1/r_m^3}.$$

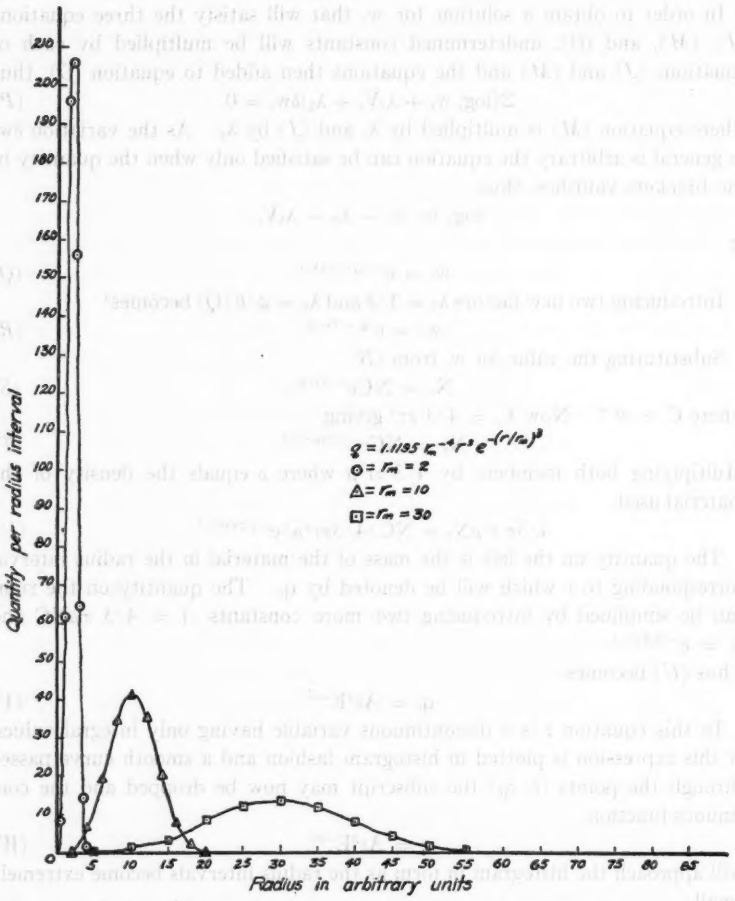


FIG. 1. GRAPHS OF DISTRIBUTION FUNCTION WITH THREE DIFFERENT VALUES OF r_m

And equation (W) becomes

$$q = Ar^3e^{-(r/r_m)^3}. \qquad (Y)$$

It is obvious that the area under the curve of (Y) is equal to the mass M of the material used.

By integration it is found that

$$M = Ar_m^4\,\Gamma(4/3)$$

or[5]

$$A = M/r_m^4\,\Gamma(4/3). \qquad (Z)$$

If M is made equal to unity $A = 1.1195\,r_m^{-4}$, which leads to an equation with one parameter.

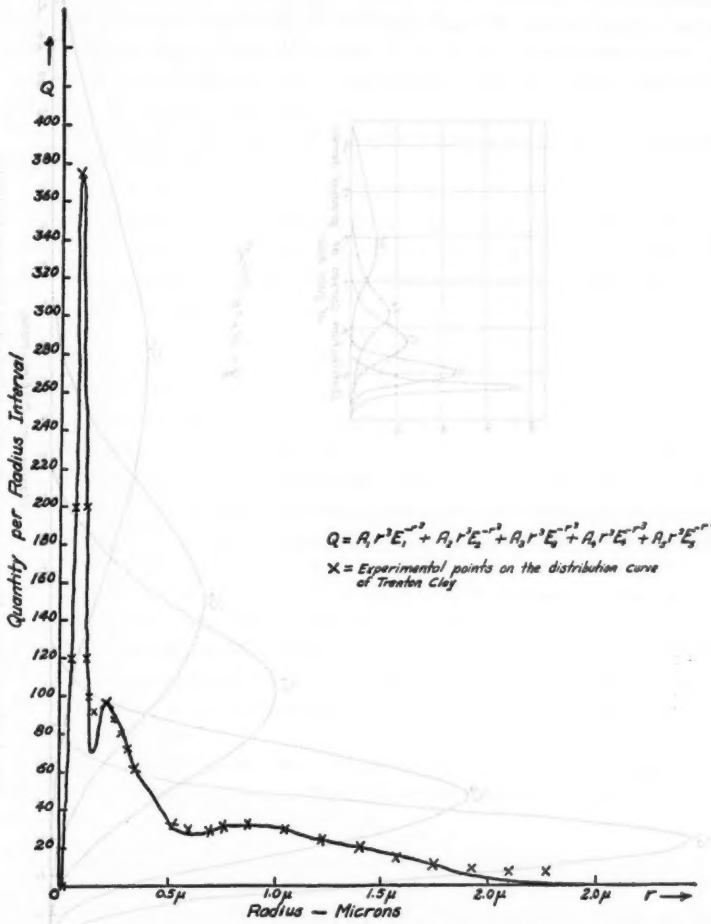


FIG. 2. COMPARISON BETWEEN THEORETICAL SYNTHETIC CURVE AND EXPERIMENTAL RESULTS

$$q = 1.1195\,r_m^{-4}\,r^3 e^{-(r/r_m)^3} \qquad (AA)$$

This equation is an expression for the most probable distribution that may

[5] $\Gamma(4/3)$ is the Gamma function of (4/3).

$$\Gamma(n) \equiv \int_0^\infty x^{(n-1)}\,e^{-x}dx.$$

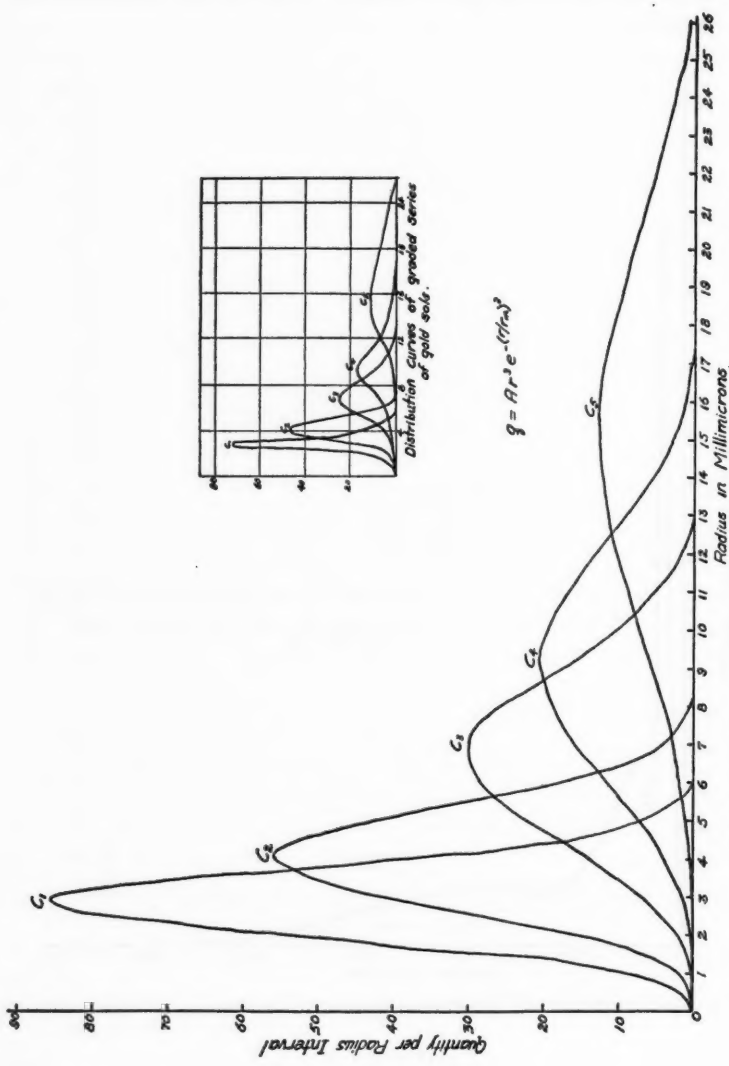


FIG. 3. THEORETICAL DISTRIBUTION CURVES OF GOLD SOLS SHOWN IN INSET

arise when a unit quantity of a homogeneous material is broken into small particles by a random process.

Figure 1 presents three plots of the expression with different values for r_m.

It is apparent that none of these curves in general would fit soil-distribution curves. In the case of soils, however, it must be remembered that instead of being composed of a homogeneous material there are several kinds of material with different physical properties each of which has a distribution curve of its own. For an example of this, a distribution curve of Trenton clay[6] is presented by the crosses in figure 2.

By summing several terms of the type given in equation (Y) resulting in an equation of the form

$$q_1 + q_2 \ldots . + q_n = A_1 r^3 e^{-(r/r_m)^3} \ldots . + A_n r^3 e^{-(r/r_{m_n})^3} \qquad (BB)$$

it should be possible to fit approximately this curve. In order to do this it seemed convenient to select the r_m's, then solve for the A's by introducing as many linear equations as there are r_m's, these equations being obtained by passing the curve through the points

$$(r_{m_1}, Q_1), (r_{m_2}, Q_2), \ldots . (r_{m_n}, Q_n)$$

where $Q_1, Q_2, \ldots . Q_n$ etc., equal the ordinates of the experimental curve with the respective abscissas $r_{m_1}, r_{m_2} \ldots . r_{m_n}$.

Figure 2 shows that there are three noticeable maxima. By passing the theoretical curve through these three points, thus letting $n = 3$ and then subtracting this curve from the experimental curve, two new maxima are obtained. Using these and repeating the above process with $n = 5$ a close fit results which is shown by the solid line in figure 2. It is clear that by adding subsequent minor distributions a more precise fit may be obtained.

The two sets of curves presented in figure 3 illustrate how (Y) may represent the experimental facts when only one material is distributed. The inset curves are distributions of a series of graded gold sols obtained by Rhinde.[7] The other curves are plots of (Y) with the constants chosen so as to make the r_m's the same as in the experimental distributions and the ordinates of the maxima proportional.

It would seem, therefore, that a consideration of the theory of probability leads to a rational equation representing distribution curves of dispersed materials.

[6] JENNINGS, D. S., THOMAS, M. D., AND GARDNER, W. 1922 A new method of mechanical analysis of soils. *Soil Sci.* 14: 485–499.

[7] NICHOLS, J. B. 1932 *The ultracentrifuge and its field of research. Indus. and Engin. Chem.* (Analyt. Ed.) 4: 12–17. *Original Reference:* RHINDE 1928 Distribution of Sizes of Particles in Gold Sols, p. 145–165 Dissertation (Upsala, Sweden). (Not seen.)

arise when a unit quantity of a homogeneous material is broken into small particles by a random process.

Figure 1 presents three plots of the expression with different values for α. It is apparent that none of these curves in general would fit well-distribution curves. In the case of soils, however, it must be remembered that instead of being composed of a homogeneous material there are several kinds of material with different physical properties each of which has a distribution curve of its own. For an example of this, a distribution curve of Trenton clay is presented by the crosses in figure 2.

By assuming several terms of the type given in equation (7) resulting in a series of the form

it should be possible to fit any arbitrary distribution curve. In order to do this it is proposed hereinafter to select the p_i so that only two of the A's be different from zero, thereby greatly limiting the number of unknowns. These equations being obtained by passing the curve through the points

where (p_1, Q_1) and (p_2, Q_2) are equal the ordinates of the experimental curve with the respective abscissas x_1 and x_2.

Figure 2 shows that there are three noticeable maxima. By passing the theoretical curve through these three points, thus letting $n = 3$ and then solving the three equations for the exponents curve, two sets of maxima are obtained. Using these and repeating the above process with $n = 5$ a close fit results which is shown by the solid line in figure 2. It is seen that by adding subsequent terms distributions even more precise than this can be obtained.

The application of curves presented in figure 1 illustrate how (7) may represent the experimental facts when only one material is distributed. The next curves are distributions of a series of graded soil obtained by Rhinde. The other curves are plots of (7) with the constants chosen so as to make the p_i's the same as in the experimental distributions and the ordinates of the maxima proportional.

It would seem therefore that a consideration of the theory of probability could be a rational guide to a general equation representing distribution curves of dispersed materials.

[Illegible] Trans. 21 (1) [illegible] R. 1912. A new method of mechanical analysis. 1: 189–235.

Rhinde, P. H. 1925. The determination of fall of rivers. Indic. and Engin. [illegible] 2: 43–72. Chemical Abstracts. 1926. Distribution of size of particles in soils. 20: 125. Distribution (Trenton clay soil). 2561 (1926).

THE CARBON-NITROGEN RATIO IN RELATION TO SOIL CLASSIFICATION

M. S. ANDERSON AND HORACE G. BYERS

Bureau of Chemistry and Soils, U. S. Department of Agriculture

Received for publication August 29, 1933

In a recent bulletin (4) the writers have called attention to the marked differences in the properties of organic matter derived from podzols and from prairie and other dark colored soils. They have also (10) called attention to the relationship between the chemical properties of the inorganic soil colloids and the great soil groups, as developed by Marbut and his co-workers (18, 19), in the study of the field characteristics of soils. This relationship has been more fully developed for the inorganic colloids in subsequent publications (6, 7, 9).

It is of great interest to ascertain whether the organic colloid of soils is likewise differentiated by climatic influences and is a variable material, not only in quantity but in character in different soils. The analytical data on the organic matter of soils is very meager except in two respects: the carbon content of the soil and the nitrogen content. The determination of these two components is relatively easy and with proper prccautions may be very exact, and many reports are available which deal with them. The value of many of these is greatly lessened, for our present purpose, by reason of the apparent impossibility of differentiating between charcoal and coal particles and soil organic matter, and because but few of the investigations have been so carried out that horizontal differentiation can be considered. It seems probable also that some of the carbon determinations have been reported without due attention to the possible presence of carbonate. Soil classification is based upon profile characteristics and not alone on surface soil. It seemed probable, however, that sufficient usable data are available to ascertain whether the carbon-nitrogen ratio reveals any soil group characteristics.

This ratio has long been considered an important characteristic. Indeed, it was for a time, and apparently by some still is, considered sufficiently constant so that the nitrogen determination may serve as a means of estimating the organic content of a soil (16).

This assumption has repeatedly been shown to be invalid (15) and its use undoubtedly persists because within limited areas it has been found that the ratio is fairly constant for surface soils. Indeed, G. W. Robinson (22) in his text book says, on page 136, "The organic matter of soils contains carbon and nitrogen in the approximate ratio of 10:1" and on page 142, "For the soils of

the temperate regions the ratio approaches very closely 10:1." It is true that he also states, on page 352, "As a measure of soil organic matter it [the determination of nitrogen] is highly untrustworthy. . . . . It may yet prove a valuable aid to the definition of soil groups." Jenny (11) states that the ratio widens with decreased temperature and narrows with increase of temperature. He gives a range between 9:1 and 13:1. McLean (18), on the other hand, finds the ratio much higher in certain tropical soils than in England. An average of 11 tropical soils shows a ratio of 15.2 with a range between the limits of 23.0 and 9.0, while 43 English soils have a mean ratio of 9.7. It would appear, therefore, that an examination of existing data might be useful for general purposes as well as to determine whether those conditions which produce the differentiation shown by the great soil groups also produce a recognizable variation in the carbon-nitrogen ratio.

EXPERIMENTAL DATA

Before entering upon a critical examination of the data presented in the following tables attention must be directed to a few considerations concerning the determinations themselves and the resulting ratios. In the determination of organic carbon there are a number of uncertainties which materially affect the results. It is known that the carbon-nitrogen ratio of plant residues is very variable and may be as high as 80, and even in nitrogen-rich material, such as legumes, is about 20. In the determination of the soil carbon it is often uncertain how much of this undecomposed material is present and it is certainly clear that such material is not *soil* organic matter in the ordinary sense. In making carbon determinations it is customary to neglect any carbon dioxide arising from carbonates except when fairly large quantities are present, yet it has been shown (1) that rather appreciable quantities of carbon dioxide are present even in acid soils. Even when present in large quantities the methods used for its determination, while sufficiently accurate for most purposes, are still inexact enough to make the correction employed for carbon sufficiently uncertain to make material differences in the carbon-nitrogen ratio. The determinations cited in the following are made without reference, in many cases, to horizons, and therefore the differences shown by "soil" and "subsoil" are not as great as probably exist between A and B horizons. Although some investigators have considered only virgin soils, in most cases cultivated areas have been studied with the primary purpose of determining the effect of cultivation upon the organic soil content. In many cases it is not known whether virgin or cultivated soils are reported. No attempt is therefore made to segregate the data on this basis. It may be noted, however, that the work of Sievers (25) and others shows that uniform cultural treatment of soils tends to diminish the variation of the carbon-nitrogen ratio.

Finally, it is to be noted that as a given profile deepens the organic matter and nitrogen both decrease in quantity and in many cases the unavoidable experimental errors mask the relations sought. With these considerations in

mind it will be seen that any general relations shown by the data given in the following have an added interest.

The Chernozem soils

The data selected to show the carbon-nitrogen ratio for Chernozem soils are collected from various publications, as indicated in table 1, and from certain unpublished data on file in the Division of Soil Chemistry and Physics. It is probable that some of these profiles are really developed in areas more arid than correspond to true chernozem soils but it is believed that no serious error is made by their inclusion. Only soils are included from which more or less definite profile data may be obtained.

Since in part the samples included in table 1 were examined analytically for purposes quite different from that of the present study, and some of them are not subdivided by horizons and others present subdivisions of horizons, it is difficult to summarize the results in a manner not open to criticism. If, however, we select all values for samples which are wholly above 10 inches in depth, and arbitrarily take the average of these as the average ratio for the topsoil, we obtain a ratio of 9.0, with a maximum of 10.9 and a minimum of 7.5. This degree of constancy is very remarkable in view of the wide variation in carbon content. For the next layer of soil which lies between a minimum and a maximum depth 5 to 20 inches the mean value is 7.6, with a maximum of 9.3 and a minimum of 5.3. For the next layer, at depths ranging from 18 to 40 inches, the mean ratio is 6.7 with a maximum of 9.4 and a minimum of 3.9. The ratios below these depths, and indeed some of those above them, have qualitative significance only since the quantities of both nitrogen and carbon are so small that no great reliance can be placed upon the quantities reported. They do indicate, however, that the ratio is very low and decreases progressively with depth.

Because of the probable presence of undecomposed organic matter in the surface of most soils a more satisfactory comparison of the carbon-nitrogen ratios could doubtless be obtained from the colloid analyses except that in most cases ammonia has been used as a dispersing agent and the colloid acids retain ammonia when the colloid is dried. Most colloid data are therefore useless for the present purpose. In some recent work by I. C. Brown of this bureau chernozem colloids were extracted by the use of distilled water only. Table 1a contains the carbon-nitrogen ratios calculated from these analyses (7).

The profiles given in table 1a were collected from virgin soils and were subdivided to a greater degree than is usual in soil studies. They represent a series of soils in Nebraska which are produced from the same parent material—loess. The Keith silt loam is classified as a chestnut brown soil rather than as a true chernozem. The Phillips sandy loam from Montana is a solonetz soil developed under low rainfall from glacial drift.

The mean value of the carbon-nitrogen ratio for those fractions of the profiles regarded as A horizons is 9.1; for the B horizons, including all layers of

TABLE 1

Carbon-nitrogen ratios of chernozem and related grassland soils

SOIL SERIES AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO	SOIL SERIES AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Colby silty clay loam, Kans. (21)	2–10	.15	10.9	Rocky Ford fine silt loam, Colo. (15)	0–8	.11	8.2
	10–20	.07	9.2		8–13	.08	7.9
	20–33	.04	9.4		13–24	.03	7.0
	33–47	.03	6.2		24–36	.03	6.3
	47–60	.03	2.8				
	60–72	.03	2.7	San Luis sandy loam, Colo. (15)	0–10	.70	7.5
					10–24	.50	5.3
					24–36	.30	4.2
Prowers clay, Colo. (15)	0–8	.14	9.1				
	8–18	.11	7.9	Jordan sandy loam, Utah (0)	0–10	.13	8.3
	18–24	.07	7.1		10–22	.07	6.5
	24–36	.05	7.2		22–36	.05	5.7
Prowers loam, Colo. (15)	0–9	.14	8.5	Crete silt loam, Nebr. (7)*	0–1½	.13	8.9
	9–18	.08	7.5		1½–4	.15	9.3
	18–36	.05	6.0		4–20	.17	7.5
					20–38	.10	5.2
Prowers clay loam, Colo. (15)	0–9	.16	8.0				
	9–20	.09	7.5	Hastings silt loam, Nebr. (7)*	0–6	.22	9.2
	20–36	.05	6.2		6–20	.15	8.5
					20–30	.08	4.4
Prowers clay loam, Colo. (15)	0–8	.15	9.0		30–43	.07	5.0
	8–18	.08	7.6				
	18–24	.06	5.3	Amarillo silty clay loam, Tex. (3)*	0–5	.13	9.0
	24–36	.04	7.1		10–20	.08	8.0
					30–40	.06	5.0
Prowers clay loam, Colo. (15)	0–8	.21	9.5	Fillmore silt loam, Nebr. (7)*	0–2	.33	9.5
	8–18	.09	8.3		2–6½	.21	8.0
	18–36	.08	3.9		6½–16	.12	5.8
Las Animas clay, Colo. (15)	0–8	.10	8.2	Holdrege silt loam, Nebr. (7)*	0–4	.22	9.2
	8–18	.07	8.1		4–7	.18	10.9
	18–24	.04	7.2		7–18	.15	9.3
	24–36	.04	7.2		18–30	.08	5.8
Manville silt loam, Colo. (15)	0–8	.10	8.8	Charbon loam, N. Dak.†	0–1½	.23	9.3
	8–18	.09	9.3		1½–5	.16	9.1
	18–36	.03	8.3		5–13	.10	5.7
Rocky Ford fine silt loam, Colo. (15)	0–8	.13	9.3				
	8–15	.11	7.4				
	15–36	.05	5.1				

* Carbon values calculated by taking 58 per cent of the organic matter content determined by H_2O_2.

† Unpublished data.

TABLE 1a

*Carbon-nitrogen ratios of colloids extracted from chernozem soils**

SOIL SERIES AND LOCATION	DEPTH	HORIZON	C†	N	C:N RATIO
	inches		*per cent*	*per cent*	
Fillmore silt loam, Nebraska	0–2	A_1	7.38	.70	10.5
	2–6½	A_2	4.42	.33	13.4
	6½–16	B_1	1.19	.14	8.5
	16–38	B_2	1.07	.12	8.9
	38–42	B_3	0.85	.12	7.1
	42–60	B_4	0.64	.13	4.9
	60–84	B_5	0.55	.08	6.9
	84–96	C	0.31	.07	4.4
Crete silt loam, Nebraska	0–1½	A_1	3.82	.42	9.1
	1½–4	A_2	4.16	.44	9.5
	4–20	A_3	3.86	.44	8.8
	20–38	B_1	1.32	.18	7.3
	38–60	B_2	0.64	.14	4.6
	64–84	C	0.53	.13	4.1
Hastings silt loam, Nebraska	0–6	A_1	4.17	.45	9.3
	6–20	A_2	3.42	.36	9.5
	20–30	B_1	1.36	.18	7.6
	30–43	B_2	0.86	.12	7.2
	43–57	B_3	0.59	.05	11.8
	57–78	B_4	0.50	.06	8.3
	78–108	C	0.63	.07	9.0
Holdrege silt loam, Nebraska	0–4	A_1	4.34	.51	8.5
	4–7	A_2	5.28	.55	9.6
	7–18	A_3	3.67	.41	9.0
	18–30	B_1	1.37	.16	8.6
	30–49	B_2	0.94	.17	5.5
	49–72	B_3	0.45	.12	3.8
	72–96	C	0.70	.13	5.4
Keith silt loam, Nebraska	0–½	A_1	3.09	.37	8.4
	½–3½	A_2	3.67	.48	7.6
	3½–14	B_1	3.29	.31	10.6
	14–21	B_2	1.73	.23	7.5
	21–33	5	0.97	.16	6.1
	33–40	6	1.02	.14	7.3
	40–48	7	1.08	.08	13.5
	48–72	8	0.74	.13	5.7
	72–96	9	0.52	.10	5.2
Phillips sandy loam, Montana	0–1½	A_1	5.97	.80	7.5
	1½–4	A_2	4.33	.59	7.3
	4–9	B_1	2.38	.35	6.8
	9–19	B_2	1.50	.21	7.1
	19–36	B_3	1.54	.20	7.7
	36–54	B_4	0.79	.11	7.2
	54–64	C	0.90	.11	8.2

* Data taken from a manuscript by Brown, Rice, and Byers (7).

† Carbon values calculated by taking 58 per cent of the values given for organic matter.

the Keith except the lowest, it is 7.5. The mean for the six C horizons is 6.1. These results are of great interest despite the rather wide variations in individual analyses. They demonstrate very clearly that the chernozem[1] normal carbon-nitrogen ratio is materially less than that of soils of the humid areas and that the ratio decreases with depth. The significance of these results will be considered in the general discussion (q.v.).

A further indication of the general character of the organic matter of colloids of the chernozem type is found in the colloid of the Colby silty clay loam of the Kansas erosion station (21). The ratios are 7.9 for 2 to 10 inches; 6.1 for 10 to 20 inches; 4.0 for 20 to 33 inches; and 3.4 for 33 to 47 inches.

Prairie soils

A large number of analyses of the carbon and nitrogen of soils of the prairie type are available. The greater number of those given in table 2 are taken from the work of Brown and O'Neal (8), whose analyses are reported in graphic form. The calculations made from the graphs are not strictly accurate to the first decimal place but are sufficiently accurate for the present purpose. Data for prairie soils are also available from Illinois, Missouri, and Nebraska.

A weighted average of the Iowa soils given in table 2 shows for the surface 7 inches a ratio of 12.2; for 7 to 20 inches, 11.5; and for 20 to 40 inches, 11.1. The two complete profiles from Bethany, Missouri, and Lincoln, Nebraska, show even more sharply the decrease in the ratio with increase in depth. Two very interesting profiles of prairie soils are not included in the table. One of these is the Marshall silt loam from the Erosion Experiment Station near Clarinda, Iowa (21). The carbon-nitrogen ratios for this soil are 9.8 for 0 to 13 inches, 10.2 for 13 to 24 inches, 7.9 for 24 to 45 inches, and 6.2 for 45 to 71 inches. This profile is from an area long cultivated and subjected to erosion. It offers an interesting example of an effect of erosion on organic matter. The other profile of special interest is a Palouse silt loam from the Erosion Experiment Station near Pullman, Washington. The Palouse soils are described by Marbut (19) and definitely classified as chernozem soils. Yet the analyses of the erosion station soil and its colloid reveal no chernozem characteristics as indicated by the silica ratios or carbonate accumulation, at least to a depth of 75 inches (21). The carbon-nitrogen ratios are, however, 9.7 for 0 to 20 inches, 4.6 for 20 to 33 inches, 5.3 for 33 to 62 inches, and 5.2 for 62 to 75 inches. These ratios are very distinctly of the chernozem type (*see* table 1). The corresponding ratios for the colloid are 6.9, 6.5, 4.8, 3.3, and 3.0, and those for the colloid of the Shelby soil profile given in table 2 are 9.3, 7.9, 4.9, 3.4, 4.1, and 5. It can not be concluded, however, that the carbon-nitrogen ratios are always smaller for the colloids than for the corresponding

[1] It is to be noted that tables 1 and 1a include soils which have developed under short grass cover and are not all true chernozems.

soils. The ratios for the colloid of the same Marshall silt loam profile cited in the foregoing for the soil are 10.4, 10.3, 7.3, and 6.8.

Podzol soils

There is not available at present a sufficient number of profile analyses of podzol soils to give a very definite estimate of the carbon-nitrogen ratios of the group. The material at hand is included in table 3.

In addition to these determinations, two series of podzols from Quebec

TABLE 2

Carbon-nitrogen ratios of prairie soils

SOIL SERIES AND LOCATION	DEPTH	C:N RATIO	SOIL SERIES AND LOCATION	DEPTH	C:N RATIO
	inches			*inches*	
Average of 9 profiles (8)	0–7	11.9	Average of 6 profiles (8)	0–7	11.9
Calhoun silt loam, Ia.	7–20	10.8	Waukesha loam, Ia.	20–40	12.9†
	20–40	10.1			
			Average of a group (26)	Surface	12.1
Average of 9 profiles (8)	0–7	13.3	of 83 silt loam soils of	Subsurface	11.5
Grundy silt loam, Ia.	7–20	12.8	Illinois	Subsoil	8.9
	20–40	11.5			
			Average of a group (26)	Surface	11.7
Average of 15 profiles (8)	0–7	12.1	of 16 black clay loam	Subsurface	11.9
Clinton silt loam, Ia.	7–20	10.5	soils of Illinois	Subsoil	9.0
	20–40	9.9			
			Shelby silt loam (21),	0–7	11.7
Average of 10 profiles (8)	0–7	12.3	Bethany, Mo.	8–12	11.4
Tama silt loam, Ia.	20–40	11.0		12–20	10.2
				20–24	6.8
Average of 4 profiles (8)	0–7	10.6		24–48	5.2
Marshall silt loam, Ia.*	20–40	8.4		48–60	4.1
Average of 6 profiles (8)	0–7	12.7	Soil profile (2) near Lin-	0–12	12.6
Muscatine silt loam, Ia.	20–40	10.5	coln, Neb.	12–24	12.5
				24–36	12.2
Average of 4 profiles (8)	0–7	12.7		36–48	10.0
Webster loam, Ia.	20–40	11.9		48–60	7.3
				60–72	5.2

* One of these samples differs widely from the others, being abnormally high in nitrogen.

† One of these subsoil samples is abnormally low in nitrogen.

Province, Canada, are reported by McKibbin and Gray (17). One series of "upland podzols," eight in number, give a mean carbon-nitrogen ratio of 21.4 for the surface soil and 19.3 for the subsoil. Another series of "lowland podzols," eleven in number, give a mean value for the surface soil of 22.6 and 21.1 for the subsoil. The variations in both series are between wide limits. In neither series are the depth measurements indicated. No data are available for the so-called "podzols" of the pedocal type (14) nor for ground water podzols.

Only one definite conclusion can be drawn from the data. Podzol soils have a much higher mean carbon-nitrogen ratio than have either chernozem or prairie soils. It appears probable that the variation with depth is less regular and that the processes which produce podzolization also produce this irregularity (*see* general discussion).

Gray-brown podzolic soils

A very large number of determinations of the carbon-nitrogen ratio of gray-brown podzolic soils are available; unfortunately, however, only a very limited

TABLE 3

Carbon-nitrogen ratios of podzol soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN§	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Caribou loam (15), Maine	0–8	0.23	13.2	Beckett loam* (3) Mass.	0–6	1.04	16.5
	8–12	0.14	10.9		6–11	0.05	23.2
	12–18	0.08	10.0		11–13	0.14	37.6
	18–36	0.07	7.0		13–24	0.09	36.1
					24–36	0.02	40.6
Superior fine sandy loam* (3), Wisc.	0–3	1.17	20.1				
	3–8	0.04	18.8	Lakewood soil series (13), N. J.†	0–5	0.016	48.3
	12–30	0.03	27.0		5–15	0.008	15.2
	30–40	0.01	11.6		15–23	0.023	23.8
					23–40	0.024	17.8
Lakewood soil series (13), N. J.†	0–2	0.103	40.8		40+	0.008	10.6
	2–8	0.009	87.7				
	8–10	0.041	32.4	Podzol profile from Connecticut, probably Brookfield loam; depths not given‡	A_0 "F"	1.69	28.2
	10–12	0.044	27.5		A_1 "H"	1.33	29.8
	12+	0.008	33.8		A_2	0.11	23.3
					B_1	0.27	27.5
				Washburn loam (14), Maine	0–8	0.32	15.3

* Ratio calculated from organic matter by H_2O_2 method.

† Some charcoal from forest fires present.

‡ Forest soil investigations in Connecticut. M. F. Morgan, *Amer. Soil Survey Assoc. Rept. 10th Ann. Meeting Bul.* 11: 108–114 (mimeographed).

§ Samples of podzol soils are sometimes taken after elimination of the leaf mould on the surface; in other cases the leaf mould is collected and labelled the A_0 horizon. In this table the high-nitrogen samples apparently consist largely of leaf mould.

number are of profile samples, and in many cases these are profiles of cultivated soils. It is impossible, therefore, to determine to what extent the surface horizons have been affected by erosion or fertilization. A selection of these profile samples is given in table 4. Because of the predominant number of profiles from the more southern members of the group, it is not believed that this selection fairly represents the soil group.

If a weighted average of these profiles be taken we find the ratio of the A horizon to be 12.5; that of the B horizons, 10.3; and of the C horizons, 7.6. It should be noted that the data of table 4 include averages for ten profiles of Norfolk soils and nine of Sassafras. Since the detailed data are not given, the interested reader is referred to the literature cited. If these references are consulted it will be found that the nine Sassafras profiles show a fair constancy, the range being between the limits of 9.6 and 13.8. On the other hand,

TABLE 4

Carbon-nitrogen ratios of gray-brown podzolic soil profiles, including red and yellow podzolic soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Berkshale loam (15), Pa.	0–8	.18	10.2	Sassafras loam (15), Md.	0–10	.13	9.6
	8–18	.09	9.2		10–20	.03	7.4
	18–36	.05	4.1		20–36	.02	6.8
Sassafras loam (15), Va.	0–8	.07	12.4	Sassafras series (15) average of 9 profiles	A horiz.	...	11.2
	8–15	.04	7.7		B horiz.	...	8.3
	15–36	.04	5.6		C horiz.	...	6.6
Norfolk fine sandy loam (15), Va.	0–9	.06	12.4	Norfolk sandy loam (15), S. C.	0–8	.03	18.1
	9–20	.02	7.6		8–30	.01	20.0
	20–36	.02	13.3		30–36	.03	8.0
Norfolk series (15) average of 10 profiles	A horiz.	...	16.3	Vernon fine sandy loam* (21), Okla.	0–3	.70	13.0
	B horiz.	...	12.3		3–10	.21	15.4
	C horiz.	...	9.1		10–27	.15	11.6
				Rossmoyne silt loam, Ohio†	0–8	.13	11.4
					8–16	.05	9.8
					16–20	.04	6.5
					22–24	.03	7.1

* These ratios are calculated from the H_2O_2 solution loss.

† Conrey, G. W., Steele, J. G., and Green, T. C. The composition of the Rossmoyne silt loam and its extracted colloid. *Amer. Soil Survey Assoc. Rept. 10th Ann. Meeting* Bul. 11: p. 1–14 (mimeographed).

the ten Norfolk profiles show highly variable ratios, the range being from 7.1 to 26.5 with values well distributed throughout this range.

To supplement the results given in table 4 the data given in table 4a are presented. These data, taken for the most part from a paper by Robinson and Holmes (23), give the surface soil and subsoil ratios. To these are added the data for two soils taken from the work of Leighty and Shorey (15).

The mean value of the ratio for the surface soils is 12.7 and for the subsoils

10.2 Although these ratios check closely with the averages for table 4, it is to be noted that the variations are extremely wide.

It is greatly to be regretted that no data are available for the colloids of this group. There are many analyses of colloids, but in every case except one the colloids were extracted with the aid of ammonia. This is the Vernon fine sandy loam from Oklahoma (21). In this profile the colloid has a C:N ratio for depth 0 to 3 inches of 7.1; for 3 to 10 inches, 5.6; for 10 to 27 inches, 3.7; and for 27 to 58 inches, 1.5. Whether in the other colloids a like low ratio would appear is unknown.

TABLE 4a

Carbon-nitrogen ratio of gray-brown podzolic surface soils and subsoils and certain red and yellow podzolic soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Chester loam (23), Va.	0–8	.07	17.4	Hagerstown loam (23), Md.	0–8	.13	6.6
	8–32	.03	15.1		8–30	.06	5.0
Clarksville silt loam (23), Ky.	0–10	.10	5.6	Manor loam (23), Md.	0–7	.11	10.8
	10–36	.04	12.3		7–20	.03	26.6
Huntington loam (23), Md.	0–8	.20	11.2	Ontario loam (23), N. Y.	0–12	.18	9.2
	8–30	.20	2.9		12–22	.04	8.7
Miami silty clay loam (23), Ind.	0–10	.09	10.6	Norfolk fine sandy loam (23), N. C.	0–8	.06	23.2
	10–24	.07	10.7		12–36	.04	5.7
Sassafras silt loam (23), Md.	0–8	.07	12.6	Marlboro sandy loam (15), N. C.	0–5	.055	18.0
	8–22	.03	8.6		12–18	.025	8.0
Portsmouth sandy loam (15), S. C.	0–8	.055	14.5				
	8–36	.027	8.9				

The lateritic soils

It should be noted that Marbut (10), in his former classification, does not recognize the existence of a lateritic great group, but, instead, he separates the soils of the southern humid area into yellow and red soils, which are podzolic in character in most cases. The examination of the colloids of these soils shows that some of them have silica-sesquioxide ratios of 2 or more. These we have included, so far as they are known, with the gray-brown podzolic soils in tables 4 and 4a, even though they may be yellow, as in the case of the Norfolk, or red, as in the case of the Vernon. The soils included in table 5 are either truly lateritic, with a silica-sesquioxide ratio for the colloids of below 2, or closely related to lateritic soils.

Table 5 shows no such wide variations in the carbon-nitrogen ratio as appear

in the podzol and podzolic groups. The mean value of the ratio for the A horizon is 15.2; for the B horizon, 10.8; and for the C horizon, 7.9. The high average of the surface soil is undoubtedly due to undecomposed organic matter.

TABLE 5

The carbon-nitrogen ratio of the lateritic group of soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Kirvin fine sandy loam (21), Tex.	0–12	.04	7.8	Nacogdoches fine sandy loam; Tex.*	0–8	.10	11.0
	12–24	.05	9.4		8–18	.06	11.0
	24–51	.02	7.0		18–40	.03	8.0
Cecil sandy clay loam (21), N. C.	0–6	.09	20.7	Cecil clay loam (23), Ga.	0–9	.03	10.8
	6–32	.04	6.5		9–18	.04	15.7
	32–60	.04	4.9				
				Cecil fine sandy loam (15), N. C.	0–10	.04	13.6
Cecil sandy loam (15), N. C.	0–8	.03	17.3		10–18	.03	10.9
	8–15	.03	13.3		18–36	.02	6.6
	15–36	.02	12.7				
				Greenville fine sandy loam (15), Ga.	0–8	.032	18.4
Davidson clay loam (15), N. C.	0–7	.07	16.9		8–15	.032	13.7
	7–12	.06	12.7		15–36	.026	8.4
				Dunbar fine sandy loam (15), N. C.	0–8	.07	15.0
Greenville sandy loam (15), Ga.	0–10	.036	15.2		8–18	.02	8.0
	10–15	.026	11.1		18–36	.03	5.9
	15–36	.023	7.4				
				Orangeburg fine sandy loam (23), Miss.	0–10	.03	14.9
Appling sandy loam (15), N. C.	0–8	.04	21.1		10–36	.03	6.6
	8–18	.03	12.6				
	18–36	.02	10.5				

* Unpublished data.

TABLE 5a

Carbon-nitrogen ratio of colloids from lateritic soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	ihches	*per cent*			*inches*	*per cent*	
Kirvin fine sandy loam (21), Tex.	0–12	.21	7.0	Cecil sandy clay loam (21), N. C.	0–6	.15	8.9
	12–24	.14	3.4		6–32	.07	2.2
	24–51	.11	1.9				

In at least one of the profiles, the Cecil sandy clay loam, visible fragments of pine needles were observed.

The colloid carbon-nitrogen ratios of two samples are available. These are given in table 5a.

No general observations can be made upon such scanty data but it is of

interest that these two colloids have a higher ratio in the soil than in the colloid of the surface horizon but the difference is much more marked in the Cecil than in the Kirvin. The lower horizons of the colloids also are sharply different from the soils.

Laterite soils

No data concerning true laterites are available for United States soils since no such soils exist, so far as is known. The only data from abroad which seem of value are furnished by McLean (18) and by Bennett and Allison (5). As previously stated, McLean reports the mean of 11 tropical soils as 15.2. Presumably these are, at least in part, laterites. The data of Bennett and Allison include the inorganic composition of the whole soil, and from this it is possible to estimate the degree of laterization from the silica content. The carbon-nitrogen ratio of the extensively laterized soils is noticeably variable. However, a group of six surface soils show a mean ratio of 15.0.

Nitrogen and carbon content

It will be noted that nearly all of the preceding tables give the nitrogen content of the soils reported. This is a matter of considerable interest, though not directly pertinent to the main purposes of the paper. An examination of the available data for the carbon content was also made. It can not be asserted that definite conclusions can be drawn. Variations within the groups are so wide as to very nearly mask group characteristics. Also, available data do not permit an estimate of the extent to which the quantities of carbon and nitrogen are affected by cultivation and erosion. It is known that, in general, cultivation decreases the organic content of soils. It is also known that the rate of this decrease is greatly influenced by climatic factors. The soils considered in this paper are partly virgin and partly cultivated. They also are from types of varying degrees of maturity. In many cases detailed information concerning the carbon content is not available and especially where horizontal data are given the horizons are not directly comparable. For these and other reasons there seems but little to be gained from attempting a detailed statement concerning the relative quantities of carbon and nitrogen.

It is of some interest to note the approximate averages of the carbon and nitrogen in the surface horizons of the great groups. These are shown in table 6.

It will be observed from the values given in table 6 that the differences among the great soil groups are very marked. The maximum content of both organic carbon and nitrogen is shown by the podzols. In this group also the average is derived from single values which are especially divergent. This wide divergence is probably due to the manner of collection of the samples. In some, the highly organic surface layer is included and in other cases is not. It seems probable that were this layer always included in the analytical data, the quantities would be more uniform and also higher. It is also true that the

organic content of the B horizon of the podzol soils is relatively very high. Whether this surface organic matter is included in the Canadian samples is unknown. The lowest carbon and nitrogen content shown in the table is for the lateritic group. It seems probable that were adequate data available the laterites would be still lower.

It seems probable that if *virgin* soils of the great soil groups were studied a more definite differentiation would appear. Especially would this be the case if the studies were made upon soils comparable in respect to maturity and to drainage conditions and with horizons properly segregated.

It is believed also that much information of value would be gained if future profile studies of both soil and colloid were so conducted as to throw additional light upon the relation between the organic content and the classification of soils. To make the best use of such data it is essential to know whether the

TABLE 6

Average carbon and nitrogen content of the surface soils of the great soil groups*

SOIL GROUP	ORGANIC CARBON	NITROGEN
	per cent	*per cent*
Chernozem	1.45	0.16
Prairie	2.50	0.20
Podzol (U. S.)	14.70	0.60
Podzol (Canadian upland)	3.30	0.15
Podzol (Canadian lowland)	5.40	0.25
Gray-brown podzolic	1.25	0.10
Lateritic	0.80	0.05

* It is to be noted the average carbon and nitrogen contents do not necessarily give a ratio which is the same as the average of the single ratios.

soils examined are virgin or cultivated and whether they have been modified by erosion or other processes likely to affect their organic content.

GENERAL DISCUSSION

In order to summarize the results given in the foregoing tables the mean values of the carbon-nitrogen ratio of the various groups are restated in table 7.

The values given in table 7 for the carbon-nitrogen ratio bring into sharp relief three points, of which two have already been emphasized by Leighty and Shorey (15). First, it is clearly evident that there is no constant ratio between nitrogen and organic carbon or total soil organic matter, either in soil or colloids. Second, the general relation is a decrease of the ratio, a relative increase of nitrogen, with increasing depth. Third, a wide divergence exists between the carbon-nitrogen ratio of the different great soil groups. Unfortunately, there is not adequate data to make certain how divergent the ratios may be within a soil series. It will be of interest to collect information upon this point, particularly from the colloids, when these are properly separated from the soil.

With respect to the first of these points little remains to be said except further to emphasize the point that however unsatisfactory the other methods of estimating soil organic matter (1) may be, certainly a determination of the nitrogen as a means of estimating carbon or organic content is about the worst, since the ratio not only varies widely from soil to soil but also varies with depth, and therefore with the degree of erosion. Whether there is also a seasonal variation is undetermined, but it seems probable. The chernozem soils, particularly the A horizon, appear to have an approximately constant ratio, though to what extent this is varied by cropping is not known. The prairie soils also have a fairly constant carbon-nitrogen ratio.

More is to be noted with respect to possible causes for the variation of the ratio with depth. The data of tables 1 to 5 show wide variations in this respect. Before general relations are considered it should be pointed out that as both carbon and nitrogen decrease in amount and the presence of small

TABLE 7

The mean carbon-nitrogen ratios of the great soil groups

GROUP	HORIZON A	HORIZON B	HORIZON C
Chernozem soils	9.0	7.6	6.7
Chernozem colloids	9.1	7.5	6.1
Prairie soils*	12.2	11.5	11.1
1 Prairie colloid	9.3	7.9	5.0
Podzol soils† (Canadian upland)	21.4	19.3	...
Podzol soils (Canadian lowland)	22.6	21.1	...
Podzolic soils	12.5	10.3	7.6
Podzolic soils	12.7	10.2	...
Lateritic soils	15.2	10.8	7.9

* The three ratios are not of true horizons; the C horizon lies much deeper.

† The values given are not horizontal but are for "soil" and "subsoil."

amounts of carbonates tends to increase, the experimental errors become a larger factor in the results reported.

One of the probable influences which produce the decrease in the ratio with increase in depth is the difference in composition of roots of plants as compared with their stems, branches, and leaves. Little definite information on this point is available. Indeed, there is a somewhat remarkable lack of information about the composition of roots. Some data on fleshy roots, such as beets and turnips, indicate a wider carbon-nitrogen ratio than for their leaves, but these are not soil-forming types of vegetation. Unpublished data of this bureau indicate that certain shrubby plants have a lower carbon-nitrogen ratio for their roots than have their tops. For the bulk of soil-forming vegetation such as grasses, cereals, weeds, and trees, no information is at hand. Since it seems probable that a large portion, at least, of the organic matter of the lower portion of the soil is formed there, it is possible that a lowered ratio of the roots is in part responsible.

A more probable influence in some cases and of one greater magnitude is the presence in the upper portions of the soil of charcoal derived from fires which incompletely consume the surface vegetation. More will be said of this in connection with the group distribution.

A third influence which undoubtedly has a large bearing upon the result is a difference in the character of the microbiological processes at and near the soil surface and at lower depths. The writers have no special information on this subject, but it would seem reasonable to assume that the processes of decay taking place at the surface and in the upper portion of the soil profile would result in different residual materials from those occurring under widely different conditions at lower levels.

In any case it appears that nitrogenous materials suffer less complete decomposition or, at least, less rapid conversion to soluble or gaseous forms than do carbohydrate residues. It is pointed out by Salter (24) that organic materials contributing largely to soil organic matter have very large carbon-nitrogen ratios and in the soil these tend to decrease toward smaller values. Thom and Humfeld (27) have shown that the number of microorganisms at the surface of soil roots is vastly greater than in the adjacent soil. This doubtless means that bacteria are utilizing high ratio material as an energy source and are producing carbon-dioxide while at the same time they build up compounds of higher nitrogen content which form bacterial remains. These bacterial remains probably form the larger fraction of soil organic matter. Surface, aerobic organisms may leave different residues than subsurface, anaerobic organisms.

Further, it may be assumed that, even as in the case of the inorganic material, translocation of organic material may occur in the soil. To what extent this occurs is wholly a matter of conjecture except in the case of the podzols, where it is clearly evident that there is large accumulation of organic matter in the B horizon. It seems probable that soluble organic matter from the surface may be precipitated at lower levels as a result of change of pH values and increased base content and this soluble material may be more highly nitrogenous than the original material from which it is separated. This statement is in harmony with the recent work of Joffe (12) on lysimeter extracts through different horizons. Also, it seems reasonable to assume that fractionation of suspended material may occur by the same processes which fractionate and translocate inorganic material; viz., suspension in colloidal form and precipitation and filtration at lower levels. In any case, the result of these or other active influences seems to be a narrowing of the carbon-nitrogen ratio with increasing depth. A study of this relation for the profiles of a given soil series, particularly with reference to colloids, would seem likely to be a fruitful topic.

When we turn to the variations of the carbon-nitrogen ratio among the great soil groups we may expect the same influences which affect the ratio with depth to be operative to a very great extent. Other considerations, however, also enter the problem. The sources of the organic matter are widely different.

In a general way we may say that the chernozem soils considered in table 1 are developed under short grass cover. Those of table 2 are high grass prairie soils Those of table 3 are developed under pine forest cover; those of table 4, under deciduous forest cover; and those of table 5, under deciduous cover and high temperature. It is shown by Salter (24) in the paper previously cited that there is a wide divergence between the carbon-nitrogen ratios of many plants contributing to soil organic matter and, although the short grasses, high prairie grasses, pine needles, and deciduous leaves are not included, there are undoubtedly wide differences. These differences should have an effect even though the trend be *toward* though not *to* a common line.

Again, the great group soils are developed under very different conditions of humidity and temperature and these conditions ought to be expected to result not only in decomposition to varying degrees but because of the differing active organisms should be expected to produce different products. The writers are not aware to what extent the microbiological population of the different soil groups is variable, but it is not a wild assumption if we expect them to be widely different.

A consequence of the different types of vegetation is the difference in the probable presence of charcoal in the soil. In the dry, short grass country, fires are relatively rare and because of the dryness when they do occur the combustion of the organic matter is more likely to be complete. In the high grass prairies the fires are likely to be more frequent and to leave more unconsumed charcoal of small particle size. In the forested areas the natural forest fires and those carried on in clearing operations may cause large variations in carbon content in local ports. Indeed, two of the profiles given in table 3 are known to be so affected.

An influence of unknown magnitude as affecting the data presented in this paper is the extent to which the decomposition of the plant residues is complete. Surface soils in particular may have practically undecomposed fragments of leaves, pine needles, and straw fragments which raise the carbon-nitrogen ratio, and if the same soil be sampled when or where such fragments are not present, the results obtained would be different. It is believed that this is the chief cause of the differences between the surface soil ratios of the Cecil soils in table 5. This is indicated by the ratio shown by the surface colloid, as compared with the soil from which the colloid was extracted.

The carbon-nitrogen ratio of soils is probably also affected by the texture of the A and B horizons, the presence or absence of claypans and hardpans, the extent of erosion, and other influences which determine where and to what extent the organic residues of organic matter are deposited. It is also probable that the ratio is seriously modified seasonally, not only by reason of seasonal production of nitrates, nitrites, and ammonia and their removal through crop growth and drainage but also as a result of the decay, or its lack, of carbohydrates and related compounds.

In considering the rather striking general relations shown in table 6 it must

not be forgotten that the individual soils in each group, except possibly the chernozem and prairie groups, show very wide variation from the mean, and that nothing is presented in general as indicating the causes of these variations.

Despite all these qualifications, however, the writers believe that the results indicate a definite difference in the general character of the soil organic matter in the different groups, and they propose further study along this line in the hope that as additional data are assembled light may not alone be thrown upon the causes of variation but upon the chemical composition of the product. It would be helpful if soil students, when dealing with profile studies whether of soil or colloid, were to make careful record of both total carbon and total nitrogen content.

SUMMARY

A study is made of the available data on the carbon-nitrogen ratio of soils with reference to their classification in the great soil groups. In each group the ratio decreases with depth, though this decrease in neither uniform nor absolutely general. The mean nitrogen content of the surface soils of the great soil groups is also given.

The variations of the carbon-nitrogen ratio are so wide as to make the determination of nitrogen wholly useless as means of estimation of either carbon or organic matter.

The data indicate a wide variation in the ratio between the great groups and also a highly variable ratio in different soils within each group. The most constant ratio is found in the chernozem group. It is more variable in the prairie group and becomes erratic in the other groups.

The possible and probable factors which determine the magnitude of the ratio are discussed, and the conclusion is reached that the results indicate an essential difference in the organic matter of the different groups. The need of study of this relation, particularly with reference to definite soil series and their colloids, is indicated and cooperation is asked.

REFERENCES

(1) ALEXANDER, L. T., AND BYERS, H. G. 1932 A critical laboratory review of methods of determining organic matter and carbonates in soil. U. S. Dept. Agr. Tech. Bul. 317.

(2) ALWAY, F. J., AND VAIL, C. E. 1912 The relative amounts of nitrogen and humus in some Nebraska soils. *Nebr. Agr. Exp. Sta. Ann. Rpt.* 1912: 145–163.

(3) ANDERSON, M. S., AND BYERS, H. G. 1931 Character of the colloidal materials in the profiles of certain major soil groups. U. S. Dept. Agr. Tech. Bul. 228.

(4) ANDERSON, M. S., AND BYERS, H. G. 1933 Character and behavior of organic soil colloids. U. S. Dept. Agr. Tech. Bul. 377.

(5) BENNETT, H. H., AND ALLISON, R. V. 1928 The Soils of Cuba. Washington, D. C.

(6) BROWN, I. C., AND BYERS, H. G. 1932 The fractionation, composition and hypothetical constitution of certain colloids derived from the great soil groups. U. S. Dept. Agr. Tech. Bul. 319.

(7) BROWN, I. C., RICE, T. D., AND BYERS, H. G. 1933 A study of claypan soils. U. S. Dept. Agr. Tech. Bul. 399.

(8) BROWN, P. E., AND O'NEAL, A. M. 1923 The color of soils in relation to organic matter content. *Iowa Agr. Exp. Sta. Res. Bul.* 75: 275–300.

(9) BYERS, H. G. 1933 The constitution of the inorganic soil colloids. *Rept. 13th Ann. Meeting Amer. Soil Survey Assoc. Bul.* 14: 47–52.

(10) BYERS, H. G., AND ANDERSON, M. S. 1932 The composition of soil colloids in relation to soil classification. *Jour. Phys. Chem.* 36: 348–366.

(11) JENNY, H. 1929 Relation of temperature to the amount of nitrogen in soils. *Soil Sci.* 27: 169–188.

(12) JOFFE, J. S. 1933 Lysimeter studies: III. The movement and translocation of nitrogen and organic constituents in the profile of a podzolic soil. *Soil Sci.* 35: 401–411.

(13) JOFFE, J. S., AND WATSON, C. W. 1933 Soil profile studies: V. Mature podzols. *Soil Sci.* 35: 313–331.

(14) LEHAY, A. 1932 Leaching of mineral matter in some Alberta soils. *Sci. Agr.* 13: 7–15.

(15) LEIGHTY, W. R., AND SHOREY, E. C. 1930 Some carbon-nitrogen relations in soils. *Soil Sci.* 30: 257–266.

(16) LYON, T. L., AND BUCKMAN, H. O. 1929 The Nature and Properties of Soils. New York.

(17) MCKIBBEN, R. R., AND GRAY, P. H. H. 1932 Chemical and microbiological factors in some Quebec soils. *Canad. Jour. Res.* 7: 300–327.

(18) MCLEAN, B. W. 1930 The carbon-nitrogen ratio of soil organic matter. *Jour. Agr. Sci.* 20: 348–354.

(19) MARBUT, C. F. 1927 A scheme for soil classification. *First Internatl. Cong. Soil Sci. Proc. and Papers Comn.* 5, v. 4: 1–31.

(20) MARBUT, C. F. 1933 Soils of the United States. Atlas of American Agriculture, Part 3, Advance Sheets No. 8.

(21) MIDDLETON, H. E., SLATER, C. S., AND BYERS, H. G. 1932 Physical and chemical characteristics of the soils from the erosion stations. U. S. Dept. Agr. Tech. Bul. 316.

(22) ROBINSON, G. W. Soils; Their Origin, Constitution and Classification. London.

(23) ROBINSON, W. O., AND HOLMES, R. S. 1924 The chemical composition of soil colloids. U. S. Dept. Agr. Bul. 1311.

(24) SALTER, F. J. 1931 The carbon-nitrogen ratio in relation to the accumulation of organic matter in soils. *Soil Sci.* 31: 413–430.

(25) SIEVERS, F. J. 1930 Further evidence concerning the significance of nitrogen in soil organic matter relationships. *Jour. Amer. Soc. Agron.* 22: 10–13.

(26) STEWART, ROBERT 1910 Quantitative relationships of carbon, phosphorus and nitrogen in soils. *Ill. Agr. Exp. Sta. Bul.* 145: 91–127.

(27) THOM, CHARLES, AND HUMFELD, HARRY 1932 Notes on the association of micro-organisms and roots. *Soil Sci.* 34: 29–36.

A RAPID METHOD FOR THE DETERMINATION OF TOTAL NITROGEN IN SOIL[1]

E. M. EMMERT

Kentucky Agricultural Experiment Station

Received for publication August 30, 1933

In previous papers (1, 2) a method was described for determining total nitrogen by oxidizing with sodium chlorate and sulfuric acid, distilling, and determining nitric acid in the distillate by the phenoldisulfonic-acid method. This procedure, though more rapid than the standard Kjeldahl method, requires considerable time and equipment, and the technic is rather exacting. Recent work has shown that by regulating conditions properly, distillation can be dispensed with. The nitrogen in the soil was oxidized to nitrate at 100°C. in acid solution, and the solution with an excess of chlorate present was neutralized with sodium hydroxide. The precipitated hydroxides and silica were filtered off and an aliquot of the filtrate was treated with fuming sulfuric acid to decompose and expell the excess chloric acid and to make the action of the phenoldisulfonic acid more effective by causing a high acid concentration. The phenoldisulfonic acid was then added and total nitrogen calculated from the nitrate nitrogen found. The following procedure was found satisfactory and can be completed in 10 to 15 minutes, the technic and apparatus being very simple.

PROCEDURE

To 0.2 to 1.0 gm. of finely ground dry soil (the sample should contain at least 0.5 mgm. of N) in a dry 20 x 150 mm. test tube, add by means of a pipette exactly 1 cc. of a 50 per cent solution of sodium chlorate, placing the solution in the bottom of the tube without touching the sides. Samples high in organic matter but low in nitrogen may require 2 cc. of the chlorate solution. Add exactly 3 cc. of a 50 per cent by volume solution of sulfuric acid. Shake the tube and heat the upper part of the solution while shaking until the reaction starts, but not long enough to boil off water. Put the tube into boiling water in such a manner that the water comes to the top of the solution in the tube. Keep in the boiling water until the soil is completely oxidized (usually about 5 minutes, although a longer time will do no harm). The oxidation is complete when a clear yellow or brownish solution is present with a white to brownish silica residue which settles readily. Care should be taken that appreciable

[1] The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published with permission of the director.

amounts of water are not lost from the tube, since this would make aliquoting inaccurate. Green fumes may appear and a slight explosion may take place, but this does no harm. If foaming places some particles of the soil up on the sides of the tube, they should be returned into the solution by shaking and rotating. When it is certain the oxidation is complete, cool the solution in cold water and add, slowly at first, exactly 6 cc. of 40 per cent sodium hydroxide, cooling in cold water to prevent excessive heat. The solution should now be rather strongly alkaline. Filter and place 1 cc. of the filtrate in another test tube. Add rather rapidly 2 cc. of fuming sulfuric acid (15 per cent SO_3) and shake and blow across the top of the tube until the chlorine is expelled and the solution is colorless. Boiling caused by the acid will do no harm here. Add a few drops more of the acid and note whether any more chlorine is liberated. When the solution is free of excess chloric acid, immediately add 1 cc. of phenoldisulfonic acid. The solution should remain colorless except for the tinge which the phenoldisulfonic acid adds. If a yellowish tinge appears, excess chloric acid is still present and off-color tints will appear. Another aliquot must be taken and treated as before, making certain all chloric acid is absent. If trouble is experienced in getting rid of chloric acid, heat the 1 cc. aliquot nearly to boiling before adding the fuming sulfuric acid. After a few seconds wash the solution into a 200-cc. Erlenmeyer flask with about 15 to 20 cc. of water and neutralize with clear 40 per cent sodium hydroxide until the maximum yellow color develops. Make to a volume which brings the color intensity fairly close to the standard used and compare in a colorimeter. From the nitrate nitrogen found calculate the total nitrogen in the original sample.

RESULTS

Table 1 shows the results obtained on 15 samples of soil of several types. The determinations by the Kjeldahl method were made in the regular course of work, in the laboratories of the agronomy and chemistry departments of the Kentucky Experiment Station. In computing the percentage of error, the finding by the Kjeldahl method was taken as the standard. Sample 8 was very high in manganese and low in nitrogen and still the chlorate method checked well with the Kjeldahl method.

NOTES

The fuming sulfuric acid should be of full strength. That which has become weakened by exposure to the air should not be used.

Soils high in organic matter and low in nitrogen may require more chlorate solution. The 50 per cent acid solution should be increased in proportion to the increase in chlorate solution.

It is important to heat the tube containing the soil and chlorate in acid solution over a free flame before placing in the boiling water, for if the tube is placed in the boiling water cold, chlorine dioxide is likely to accumulate before a

temperature of 100° is reached in the tube and an explosion will result which may throw out some of the solution. If the air above the tube is heated to about 100°C., chlorine dioxide will not accumulate since it is unstable above this temperature. Care must be taken, however, just to start the reaction but not to boil off any water. Since the solution is strongly acid, appreciable amounts of water will not be lost unless the temperature is raised considerably above 100°.

At first it was thought that the soil could be oxidized and the phenoldisulfonic acid added directly to the mixture after oxidation. In some cases all the nitrogen was taken up by the phenoldisulfonic acid, but especially in soils high in manganese and iron much nitrogen was lost, evidently as oxides of

TABLE 1

Comparison of total nitrogen found by the Kjeldahl and chlorate methods

SOIL NUMBER	TOTAL NITROGEN FOUND BY		PER CENT OF ERROR
	Kjeldahl method	Chlorate method	
	p.p.m.	*p.p.m.*	
1	840	846	+0.8
2	1,660	1,660	0
3	2,155	2,128	−1.2
4	1,850	1,857	+0.4
5	1,640	1,645	+0.3
6	996	988	−0.9
7	1,310	1,420	+8.4
8	310	312	+0.6
9	1,129	1,144	+1.3
10	1,728	1,711	−1.0
11	1,028	1,009	−1.8
12	1,398	1,394	−0.3
13	1,457	1,456	−0.1
14	905	905	0
15	490	420	−14.2

nitrogen. Large amounts of any heavy metals, and especially those capable of valence changes, seem to be likely to cause nitrogen losses. It has been previously noted (3) that heating nitrate solutions with silver causes appreciable losses of nitrate nitrogen. Because of these losses of nitrogen in the presence of heavy metals it was found necessary to separate the nitrogen from them.

Most of the chlorine is expelled as chlorine gas but there are some chlorides left in the acid solution. When phenoldisulfonic acid was added to a solution of the salts in a small amount of water and much sulfuric acid instead of to dry salts no loss of nitrate could be detected. A standard nitrate solution was treated with chlorate as described in the procedure and no loss was detected. The presence of a small amount of water and the application to salts in solution

overcome the loss due to chlorides which is experienced with dry salts. Evidently, nitrosyl chloride is not formed in the presence of water and as long as the acid is not diluted too much the reaction between nitrate and the phenoldisulfonic acid is complete.

On cooling, sodium sulfate may crystallize out of the neutralized yellow solution, especially if the volume is kept small. For accurate work it is best not to pour or filter off these crystals, since the hydration of the crystallized salts tends to concentrate the solution and cause high results. It is best to warm the solutions a little or keep them warm enough to prevent crystallization. In fact, the most accurate colorimetric readings are obtained immediately after dilution to the final volume, before the solution has a chance to change temperature very much and cause slight volume changes and crystallize out any salts. The same applies to the solution filtered off the soils after oxidation and neutralization. Crystals forming in the solution before the aliquot is taken may cause slight error. The solution should be kept warm enough to prevent crystallization but of course not heated so that an appreciable loss of water results.

REFERENCES

(1) EMMERT, E. M. 1929 The chlorate method for the determination of nitrate nitrogen, total nitrogen and other elements in soils and plant tissues. *Jour. Assoc. Off. Agr. Chem.* 12: 240–247.

(2) EMMERT, E. M. 1930 Procedure for determining total nitrogen by conversion to nitric acid. *Jour. Assoc. Off. Agr. Chem.* 13: 146–147.

(3) Standard Methods for the Examination of Water and Sewage, ed. 6, p. 20. American Public Health Assn., New York, 1925.

NEWER ASPECTS OF NITRIFICATION: I

G. GOPALA RAO

University College of Science, Andhra University, Waltair, India

Received for publication August 30, 1933

It is well known that ammonia, ammonium salts, and other complex nitrogenous compounds are slowly oxidized in the soil to nitrite and nitrate. This oxidation of ammonia to nitrite and nitrate is technically known as "nitrification" and is one of the most important of soil chemical processes from the point of soil fertility. It is now believed almost universally that this nitrification is in the main due to the action of nitrifying bacteria. Pasteur (12) was the first to suggest that the oxidation of ammonia is accomplished by the agency of microörganisms. This view was definitely confirmed by Schlosing and Muntz (15) and by Warington (17). After many investigators had vainly endeavored to obtain nitrifying bacteria of the soil in pure culture, Winogradsky (18) was successful. The researches of Warington and Winogradsky led to the view that nitrification was really due to the joint action of two organisms: one converts ammonia and its salts to nitrites and the other converts nitrites to nitrates but has no effect on ammonium salts.

In view of the foregoing, it is of interest to question whether the nitrification in soils is entirely due to the action of bacteria or whether it is partly due to some other agency. Gopala Rao and Dhar (6) have recently suggested that nitrification in soils must be in part purely photochemical in nature, taking place at the surface of the soil under the influence of sunlight. This view has been based on their experiments on the photochemical oxidation of ammonia and its salts in sunlight in the presence of various photosensitizers like titanium dioxide, aluminum trioxide, zinc oxide, and cadmium oxide. They have found that ammonia is oxidized to nitrite under these conditions. The present paper is devoted to the discussion of the considerable direct and indirect evidence which the author has been able to collect in favor of the photochemical view of nitrification in the soil. He has found that not only ammonium salts but also aqueous solutions of urea, acetamide, hydroxylamine hydrochloride, hydrazine hydrochloride, ethylamine, methylamine, etc. are oxidized to nitrite in sunlight under suitable conditions. It has been found that urea, acetamide, and some other substances are first converted into ammonia under the action of light, and then this ammonia appears to be oxidized to nitrite.

EXPERIMENTAL

It has been observed by several workers that ammonia is slowly oxidized in aqueous solution to nitrite when exposed to the light from a quartz mercury

vapor lamp. It has now been found that this oxidation takes place very slowly in sunlight as well. The present writer has further found that the rate of photochemical oxidation of ammonia in sunlight is increased considerably in the presence of various photocatalysts like zinc oxide, cadmium oxide, titamium dioxide, and aluminum trioxide. The ignited oxides are generally more active photocatalysts than the freshly precipitated oxides. In the presence of the basic oxides like zinc oxide, ammonium salts are also oxidized; if titania is used as a photocatalyst, only ammonia and ammonium carbonate are oxidized in aqueous solution; solutions of ammonium sulfate, chloride, etc., however, can be oxidized, if magnesium or calcium carbonate is added together with titania.

As it is very essential for the present thesis to show that the oxidation of ammonia can take place photochemically in the absence of any bacteria, rigorous precautions were taken to prevent the contamination of the reacting system by bacteria. The apparatus used for this purpose is shown in figure 1. *A* is an Erlenmeyer flask of about 2 liters capacity, fitted with a three-hole stopper. Each of the outer holes carries a piece of glass tubing bent at right angles—*B* reaching to the bottom of the vessel, and *C* just passing through the stopper. Through the middle hole passes an ordinary three-way tap, and of the three limbs *D*, *E*, and *F*, *D* reaches almost the bottom of the bottle. On *E* is blown a bulb *H* of about 20 cc. capacity and *F* is bent at right angles. *B*, *C*, and *E* are plugged with cotton wool. Thus by means of the tap, *E* can be put in communication with *D* and a sample drawn into the bulb *H*, then by suitably manipulating the tap, *D* can be cut off from *E* and the sample run off through the tube *F* into any convenient receptacle. The side tubes *B* and *C* provide a means by which the nitrifying solution can be thoroughly aerated. By attaching *B* to a series of wash bottles containing, in order, sulfuric acid, caustic soda solution, sterile water, and cotton wool it became possible to pass air (free from any nitrous gases) through the experimental solution under aseptic conditions. By this means, then, on the withdrawal of a sample, all air entering the bottle was filtered through cotton wool and the sample remained under strictly aseptic conditions until it was actually expelled from the apparatus.

Before the experiment was begun all parts of the apparatus were sterilized by steam. All solutions were made up with sterile water. In order to check the asepticity of the solutions, one solution identical in all respects with the sample exposed to light was kept in the dark. The entire absence of any reaction in the dark shows the freedom from contamination with any nitrifying bacteria. These experiments have convinced the writer that oxidation of ammonia to nitrite takes place in the entire absence of bacteria under the influence of sunlight and photocatalysts.

Methods of analysis

Modified iodometric method. For the estimation of small quantities of nitrites the permanganate method of titration is neither accurate nor delicate.

After a good number of trials the author has found that the following modification of the iodometric method of Warburg is very suitable for the estimation of minute quantities of nitrites:

To about 20 cc. of the solution were added, first, 4 gm. of sodium bicarbonate, then 5 cc. of 5 per cent potassium iodide and starch indicator solutions. A rapid stream of carbon dioxide was passed through the mixture for about 5 minutes to drive out all dissolved oxygen.

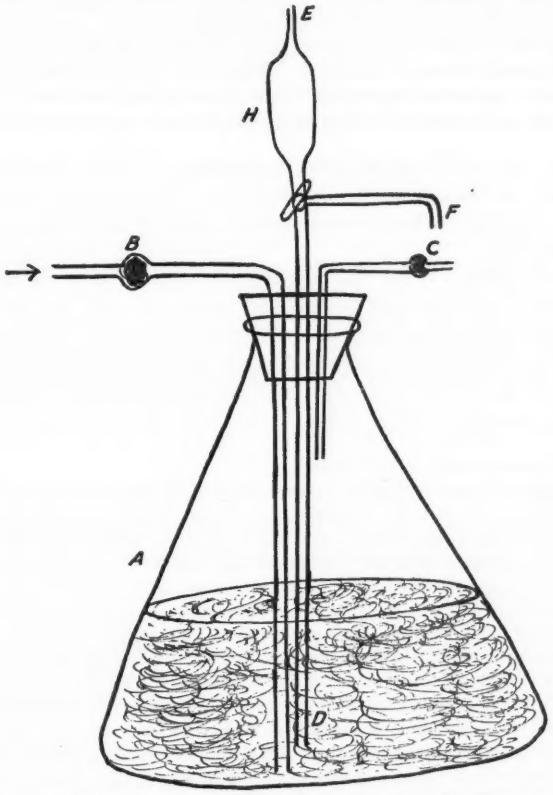


FIG. 1. APPARATUS DESIGNED TO SHOW THE PHOTOCHEMICAL OXIDATION OF AMMONIA IN THE ABSENCE OF BACTERIA

The solution was then acidified with 10 cc. of 5 *N* oxygen-free sulfuric acid, and the liberated iodine was titrated with 0.002 *N* sodium thiosulfate. The sodium thiosulfate solution was standardized against Kahlbaum's analytical potassium dichromate. This method of estimation of nitrite was checked against a standard solution of sodium nitrite prepared from pure silver nitrite.

The essential reaction in the iodometric estimation of nitrite is $2HNO_2 + 2HI = 2H_2O + I_2 + 2NO$. The liberated nitric oxide tends to be oxidized to

nitrogen peroxide, which liberates more iodine from acidified potassium iodide. Hence the amount of liberated iodine will be more than that corresponding to the equation, and the results for nitrite will be rather too high. In order to prevent the results being vitiated by this factor, two conditions must be fulfilled:

First, there should be no dissolved oxygen in the reaction mixture. This condition is obtained by passing through the solution carbon dioxide, which drives out all the oxygen and keeps the solution in an atmosphere of carbon dioxide.

Secondly, the nitric oxide should be driven out of the system as soon as it is liberated. This is accomplished by adding to the initial solution some sodium bicarbonate, which on subsequent acidification liberates large quantities of carbon dioxide simultaneously with the liberation of nitric oxide, which will therefore be driven out.

With these two conditions satisfied the amount of iodine liberated corresponds exactly to that given by the equation. The extreme sensitiveness and accuracy of this method of estimation of nitrites give it an advantage over other methods.

Colorimetric method. When the quantities of nitrites to be estimated are extremely small, however, even this method cannot be used, and resort must be made to the colorimetric methods. We know that nitrite gives an intense pink color with a solution of α-naphthylamine, sulfanilic acid, and acetic acid (Griess-Ilosvay Reaction). For the quantitative application of this method the following procedure was adopted:

Three solutions were made up and stocked.

Nitrite reagent. 0.5 gm. of sulfanilic acid was dissolved in 150 cc. of dilute acetic acid. To this was added a solution made by boiling 0.1 gr. of α-naphthylamine hydrochloride with a little water and adding enough dilute acetic acid to bring the volume up to 300 cc. This reagent should be protected from contact with air and replaced if it develops a noticeable pink color.

Glacial acetic acid.

Standard sodium nitrite solution. This was prepared from pure silver nitrite. Concentrated potassium nitrite solution was treated with silver nitrate, and the precipitate of silver nitrite obtained was filtered and washed with cold distilled water. It was then dissolved in a little hot water and rapidly cooled. The resulting crystals were filtered by suction, washed with cold water, and dried in a desiccator in the dark over calcium chloride. Then 0.1539 gm. of the pure dry silver nitrite was weighed out, dissolved in hot water, and treated with a slight excess of pure sodium chloride solution to precipitate the silver. The mixture was cooled, the precipitated silver chloride filtered off, and the filtrate diluted to 1,000 cc. This gives a standard 0.001 *N* sodium nitrite solution. As a standard for colorimetric estimations, it is diluted ten times.

About 5 cc. of the solution in which nitrite is to be estimated is run into a beaker. Then 2 cc. of the nitrite reagent and 2 cc. of glacial acetic acid are added, and the solution is made up to 40 cc. by the addition of distilled water. At the same time, to another beaker are added 2 cc. of 0.0001 *N* nitrite solution and the same quantities of nitrite reagent and acetic acid, and the solution is diluted to 40 cc. with distilled water. The contents of the two beakers are well stirred and are kept for about one-half hour until the color develops fully, after which 20 cc. of each solution is transferred into the cylinders of a Dubosq colorimeter and the amount of nitrite is estimated in the usual manner.

This method gives very considerable accuracy with higher dilutions of nitrites, but when the concentration of "nitrous" nitrogen rises above two or three parts per hundred thousand the matching of the colors becomes difficult and the accuracy of the determinations is questionable. In such cases the solution is diluted many times and the dilute solution utilized in the colorimetric determination.

Modified Devarda method. When the quantity of nitrite formed is appreciable, the estimation is best done by Allen's modification of the Devarda method. The method is based upon the quantitative reduction of nitrates and nitrites to ammonia in an alkaline solution by an alloy consisting of 45 parts of aluminium, 50 parts of copper, and 5 parts of zinc. The ammonia evolved is distilled into standard sulfuric acid and thus estimated.

EXPERIMENTAL RESULTS

Oxidation of ammonia and its salts in ultraviolet light

I have observed that ammonia is slowly oxidized in aqueous solution to nitrite, when exposed to the light from a quartz mercury vapor lamp or a copper arc and more slowly in sunlight. The nitrite can easily be detected by the color reaction given by α-naphthylamine and sulfanilic acid. Ammonium salts are also oxidized to nitrites, the reaction being slower in the case of the sulfate and chloride than in that of the carbonate.

Quantitative work in monochromatic light is in progress.

Oxidation of ammonia and its salts in sunlight in the presence of photosensitizers

We have found that the rate of the photochemical oxidation of aqueous solutions of ammonia and its salts is considerably increased in the presence of small quantities of photosensitizers like ignited titanium dioxide, zinc oxide, cadmium oxide, aluminum oxide, and silica. There is no reaction in the dark in any of these cases. Most soils contain titanium dioxide to the extent of 0.3–0.6 per cent, as shown by Geilman (5). Hence experiments done with titanium dioxide as a photosensitizer would be more pertinent from the point of soil nitrification.

To determine the effect of varying amounts of TiO_2 on the oxidation of aqueous solutions of ammonia, 100 cc. of 0.8 *N* ammonia solutions were exposed to sunlight for 20 hours in several glass bottles with varying amounts of titania. Air freed from nitrous fumes was passed through each bottle slowly at the same rate. In an ammoniacal solution titania is peptized, giving a colloidal solution which passes through the filter paper. Hence after exposure the titania was coagulated by the addition of a little barium chloride solution, filtered, and the clear filtrate made up to 100 cc. Of this liquid 20-cc. portions were taken, and the nitrite content was estimated by the iodometric method outlined in the foregoing. The results are given in table 1.

Experiments in which the same amount of TiO_2 was used with varying concentrations of ammonia gave the results shown in table 2.

TABLE 1

Effect of Varying Amounts of TiO_2 on the Oxidation of Aqueous Solutions of Ammonia

Exposure 20 hours, 100 cc. 0.8 *N* ammonia solution

AMOUNT OF TiO_2	NITRITE NITROGEN PER LITER
gm.	*mgm.*
0.006250	3.149
0.012500	6.509
0.025000	10.080
0.0500000	14.000
0.100000	18.200
0.200000	21.840
0.300000	24.600
0.400000	24.580
0.500000	24.600

TABLE 2

Effect of Varying Concentrations of Ammonia

Exposure to sunlight 20 hours, 0.1 gm. TiO_2 + 100 cc. of ammonia solution

CONCENTRATION OF AMMONIA	NITRITE NITROGEN FORMED PER LITER
	mgm.
0.32 *M*	15.530
0.16 *M*	14.700
0.08 *M*	11.270
0.04 *M*	8.399
0.02 *M*	6.789
0.01 *M*	5.040

TABLE 3

Influence of foreign substances

Exposure to sunlight 12 hours, 100 cc. of 0.8 *N* ammonia solution + 0.1 gm. TiO_2

SUBSTANCES ADDED	NITRITE NITROGEN FORMED PER LITER
	mgm.
nil	10.080
0.2 *N* sodium chloride	4.200
0.2 *N* potassium oxalate	4.200
0.2 *N* sodium benzoate	1.120
0.01 *N* sodium thiocyanate	3.080
0.5 per cent quinine sulfate	0.280

Table 3 shows the influence of foreign substances. It is interesting to note that even the addition of a neutral inorganic substance like sodium chloride

retards the velocity of oxidation of ammonia to nitrite. The mechanism of this inhibitory action will form an interesting subject for further research. The author suggests the following tentative explanation. It appears that the oxidation of ammonia takes place at the surface of the colloidal particles of titania. This is supported by the fact that ammonia is considerably adsorbed by titania. Sodium chloride coagulates the colloidal titania, causing an agglomeration of the particles, thus decreasing the available surface. Of all the substances so far studied quinine sulfate is the most active inhibitor of the photochemical oxidation. This result is easily explained by the fact that quinine sulfate is a fluorescent substance that absorbs light of short wavelength (which is responsible for the oxidation of ammonia) and degrades it into light of longer wavelength.

There is very little oxidation of ammonium sulfate in the presence of sunlight and titania, but if a basic substance like $CaCO_3$ is present besides, oxidation takes place readily. An alkaline reaction is essential for nitrite formation. In the absence of basic carbonates, only ammonium carbonate and ammonia are oxidized. In the presence of sodium, magnesium, or calcium carbonate, the sulfate, phosphate, and chloride as well as the other salts of ammonium can nitrify. The presence of a base in the medium is essential as a neutralizing agent to prevent the reaction of the medium becoming too acid as a result of the formation of nitrous and sulfuric acids from the oxidation of the ammonium sulfate.

It is interesting to note that the bacterial and photochemical nitrification processes are very similar in the foregoing aspects. In the following experiments 100 cc. of ammonium sulfate solution was exposed to sunlight for 17 hours, with 0.2 gm. of titania and 1.00 gm. of calcium carbonate. The results recorded in table 4 show that a decrease in concentration of the ammonium salt decreases the rate of formation of nitrite only to a slight extent.

The progress of the reaction of ammonia with varying lengths of exposure is shown in table 6. In this experiment, 500 cc. of 0.8 *N* ammonia solution was exposed to sunlight from day to day with 0.5 gm. of titania. Each day the exposure lasted for 5 hours, from 11 a.m. to 4 p.m. At the end of every 5 hours' exposure, 100-cc. portions of the solution were taken out and the nitrite content was estimated as usual.

Table 7 shows the effects of varying lengths of exposure of ammonium sulfate. For this experiment, 500 cc. of 0.1 *M* ammonium sulfate solution was exposed with 5 gm. of titania and 10 gm. of calcium carbonate. Every day the solution was exposed to sunlight for 5 hours. At the end of every 10 hours' exposure 100-cc. portions of the liquid were withdrawn and the nitrite content was estimated. It will be seen from the results recorded in table 7 that the amount of nitrite formed increases with time of exposure almost in direct proportion.

TABLE 4

Effect of varying the concentration of ammonium sulfate

CONCENTRATION	NITRITE NITROGEN FORMED PER LITER
	mgm.
1.00 *N*	6.299
0.50 *N*	5.948
0.25 *N*	4.899
0.125 *N*	4.200
0.03125 *N*	2.940
0.01562 *N*	2.170
0.0781 *N*	1.288
0.003905 *N*	0.6998

TABLE 5

Effect of varying the amount of titania

Exposure 20 hours, 100 cc. 0.2 *N* $(NH_4)_2SO_4$ + 1.0 gm. of $CaCO_3$

AMOUNT OF TITANIA	NITRITE NITROGEN FORMED PER LITER
gm.	*mgm.*
0.1	4.060
0.2	5.249
0.3	5.740
0.4	5.740

TABLE 6

Effect of varying lengths of exposure on ammonia

TIME OF EXPOSURE	NITRITE NITROGEN FORMED PER LITER
hours	*mgm.*
5	6.580
10	12.880
15	19.730
20	26.310
25	33.040

TABLE 7

Effect of varying lengths of exposure on ammonium sulfate

TIME OF EXPOSURE	NITRITE NITROGEN FORMED PER LITER
hours	*mgm.*
10	2.920
20	5.780
30	8.760
40	11.340
50	14.560

Comparative rates of bacterial and photochemical nitrification

The quantities of nitric nitrogen formed in the photosensitized oxidation of ammonium salts in the presence of titania and sunlight compare favorably with those obtained in the bacterial nitrification. Very recently Cutler and Mukerji (4) isolated new strains of nitrifying organisms other than Nitrosomonas. In one of their best experiments these workers obtained, with a solution of ammonium sulfate containing 0.02 gm. nitrogen per 100 cc., 0.25 mgm. of nitrite nitrogen per liter in 144 hours; whereas in the photochemical nitrification the author has obtained (table 4), with a solution containing 0.022 gm. nitrogen per 100 cc., 2.170 mgm. of nitrite nitrogen per liter in only 17 hours; in 144 hours the yield of nitrite nitrogen would have been *18.39* mgm. Under the same conditions, therefore, the photochemical process yields about 74 times more nitrite nitrogen than the bacteria isolated by Cutler and Mukerji. If we take the yield of nitrite nitrogen in a quartz vessel, it would be 200 times more.

It will be seen from the following results that the rate of photonitrification is approximately three times faster in the quartz vessel than that in the glass vessel.

	mgm. nitrite nitrogen formed per liter
100 cc. of 0.8 *N* ammonia solution exposed for 20 hours in a glass flask with 0.1 gm. of titania	18.200
100 cc. of 0.8 *N* ammonia solution exposed for 20 hours in quartz flask with 0.1 gm. of titania	52.190

To determine the effect of alumina and humic acid as catalysts of photonitrification, 100 cc. of solutions of ammonia and various ammonium salts were exposed to sunlight in glass vessels with 0.2 gm. of aluminum trioxide (Merck's) for 60 hours. The amount of nitrite formed was estimated colorimetrically, with the following results:

Substance	*mgm. nitrite nitrogen formed per liter of solution*
Ammonia 0.2 *N*	0.848
Ammonium chloride 0.2 *N*	0.747
Ammonium sulfate 0.2 *N*	0.750
Ammonium lactate 0.2 *N*	Nil
Ammonium acetate	0.090
Ammonium malonate	Nil

It was found that humic acid obtained from the soil also acts as a photocatalyst for the oxidation of ammonia to nitrite. In one case 100 cc. of 0.2 *N* ammonia solution was exposed to sunlight for 60 hours in a glass vessel with 0.1 gm. of humic acid under strictly aseptic conditions. The amount of nitrite nitrogen obtained by photo-oxidation was 0.896 mgm. per liter of solution. A control kept in the dark gave no test for nitrite. Further work is in progress on the rôle of humic acid in soil nitrification from the photochemical point of view.

Oxidation of ammonia in sunlight in the presence of sterilized soil

The final proof that nitrification in the soil is partly photochemical comes from experiments with sterilized soil as a photocatalyst. Ordinary garden soil was heated to 200°C. for several hours so as to ensure the complete destruction of all bacteria. Then it was washed several times with hot water to remove any nitrite and nitrate originally present and stirred up with an aqueous solution of ammonia. This was then exposed to sunlight in a glass or quartz vessel under aseptic conditions. Oxidation of ammonia to nitrite was always noticed. Quantitative experiments along this line are in progress.

Oxidation of urea and other nitrogenous compounds

It has also been found that various amines, amides, and amino acids are oxidized to nitrite in the presence of sunlight. The conversion of these compounds into ammonia appears to be a first stage in their final oxidation to nitrite. Aliphatic nitrogen compounds are more easily converted to ammonia than are aromatic compounds. Urea and acetamide are more readily decomposed than is benzamide, and ethylamine and methylamine are more readily decomposed than is aniline or diphenylamine. Urea hydrolyses to ammonia readily, but thiourea does not.

Amino-acids, e.g., glycine, alanine, aspartic acid, and glutamic acid, are gradually decomposed on exposure to sunlight into the corresponding aldehyde, ammonia, and carbon dioxide. In the case of glycine, formaldehyde, ammonia, and carbon dioxide are formed:

$$CH_2NH_2COOH + (0) = H{\cdot}CHO + NH_3 + CO_2$$

The ammonia thus formed is slowly oxidized to nitrite. Detailed results will be published in another paper.

DISCUSSION OF RESULTS

The experiments on the photochemical nitrification of ammonia and its salts, and many other classes of nitrogenous compounds like amides, amines, and amino-acids are remarkably interesting and point to far reaching conclusions with regard to the problem of nitrification in the soil. Hitherto it was believed that this oxidation is entirely due to bacteria, but the following facts cannot be made to fit in with the bacterial explanation:

Omeliansky and Meyerhof (10a, 11a) showed that for the bacterial nitrification process a higher concentration of ammonia or nitrite is harmful (the optimum concentration is about 0.05 per cent with a second optimum at 0.1 per cent; over 0.3 per cent interferes with the process). But in certain localities, the so-called niter spots, a high concentration of nitrite and nitrate, varying from 5–20 per cent of the bulk of the soil, has been noticed. The biological explanation cannot be entirely sufficient for the accumulation of the nitrates, as the high concentration of nitrite and nitrate should inhibit the action of the nitrifying organisms.

Several workers [Green (7), Lemmermann and Wichers (10), Jensen (9), Smith (16), and Batham and Nigam (1)] have observed a periodic variation of the nitric nitrogen con-

tent of soils. They made the important observation that the nitrifying capacity of the soil is maximum in the summer months and minimum in the winter. Experiments made in the laboratory and in the field have yielded similar results.

The curves given in Batham and Nigam's paper show that the trend of nitrate content of soils is downward from summer to winter and upward from winter to summer. The maximum solar activity occurs in the northern hemisphere in June and July and the minimum in the month of December. Accordingly the curve shows the maximum nitrate content in June–July and the minimum in December. Further it will also be seen from Batham's paper that when the average figures for the nitric nitrogen content of the autumn and spring seasons of the northern hemisphere are taken into consideration, it is found they are nearly the same, and both of them are greater than the winter figure and less than the summer one. Because the two seasons are equinoctial, the earth receives nearly the same measure of solar energy, which is greater than that received during the winter and less than that received during the summer. It will be thus seen that there is a close correlation between the solar activity and the nitric nitrogen content of the soil.

Again the northern and southern hemispheres are reciprocal in their seasons and in the lengths of their days and nights. In the southern hemisphere the solar activity is at its maximum in December and January, hence the nitric nitrogen content of the soils of the southern hemisphere must also be greatest at this time of the year. Batham and Nigam (1) have collected data of other workers to show that the nitrate content of soils of the southern hemisphere is greatest in December–January and is at its minimum in the months of June–July. Thus, as the two hemispheres are reciprocal in their seasons, they are also reciprocal in the manner of variation of the nitrate content of their soils during the different seasons of the year. More recently Prescott and Piper (13) have shown, working in South Australia, that nitrate accumulation was maximum in the months of November and December, and minimum in the months of June and July. It must be remembered that in Australia the maximum solar activity occurs in November and December, the hottest part of the year. It appears to be generally established, therefore, that nitrification is maximum in the summer and minimum in the winter.

This fact has not yet received any suitable explanation. It cannot be that sunlight stimulates the action of nitrifying bacteria, for Warington showed, several years ago, that sunlight inhibits the action of nitrifying bacteria. Besides, the high temperature reached by the soil (as high as 50° in tropical countries) is inimical to bacterial action. Hence nitrate accumulation due to bacteria should be minimum in the summer months. On the contrary it is at its maximum. This shows that there must be some other agency which also brings about nitrification, and this agency, unlike bacteria, must be favorably influenced by sunlight. Now the author has shown conclusively that the nitrification of ammonium salts and the complex nitrogenous compounds can take place in the complete absence of bacteria, if only sunlight

and photocatalysts like titania and alumina be present. Nitrification, therefore, appears to take place normally, at least to a certain extent, in the soil by the photochemical action of sunlight and soil photocatalysts like titania and alumina. Since the solar light energy is available in greater amounts in summer than in winter, the accumulation of nitrates is greatest in summer and least in winter.

It might be suggested that the periodic variation of the nitrate content of soils is due to the variation in the amount of rainfall. In the summer months there is less rainfall, and hence not much nitrate will be washed down into the lower layers of the soil. In winter months it might be that more nitrate is washed down by the greater amount of rainfall. This explanation cannot be correct in view of the following considerations. Prescott and Piper (13) have studied the distribution of the nitrate and nitrite in the various soil levels. The bulk of the nitrate and nitrite is located in the surface mulch as will be seen from table 8.

The effect of the rain is to wash down the nitrate from the surface and to redistribute this in the top 18 inches. In order to eliminate the disturbing

TABLE 8

Distribution of nitrate at different depths

DEPTH	NITRATE NITROGEN (P.P.M. OF DRY SOIL)	
	Autumn 1926	Autumn 1929
inches		
0–3½	72	73
3½–9	7	10
9–18	6	4
18–27	..	..

influence of the rain, Prescott and Piper have studied seasonal variation of the total nitrate and nitrite in the top 18 inches of the soil of various field plots. Their results, which take into account the nitrate washed down by the rain, show graphically that the nitrate nitrogen content is at its maximum in November–December (the summer months in Australia) and at its minimum in June–July (the winter months).

Nitric nitrogen also occurs in the atmosphere, as the oxides, N_2O_3 and N_2O_5, or as ammonium nitrite and nitrate. These are washed down to the earth by the rain. What is the source of this nitric nitrogen? It has been thought that oxides of nitrogen owe their origin to thunderstorms in the upper air, where, as a result the electric discharges taking place, nitrogen and oxygen combine to form N_2O_3 and N_2O_5. But be that as it may, thunderstorms do not occur often: they are the exception rather than the rule. Now if N_2O_3 and N_2O_5 are ascribed to thunderstorms, they must be washed down by the rain that follows and should be practically absent from the atmosphere on ordinary days. But this does not hold good. Air tested on any day is sure

to contain oxides of nitrogen in quantities which do not differ much from those found on days when there are thunderstorms. The amount of nitric nitrogen present at any given time does not follow the electrical disturbances in the air.

The author suggests the following explanation for the origin of nitrites and nitrates in the atmosphere. It is well known that ammonia occurs to an appreciable extent in the atmosphere, largely as a product of organic decomposition on the earth. The author has succeeded in oxidizing a solution of ammonia to nitrite by exposing it to light from a quartz mercury vapor lamp or from a copper arc. He has also shown that this oxidation of ammonia can also take place slowly in quartz vessels in ordinary sunlight. It is suggested, therefore, that the nitric nitrogen in the atmosphere owes its origin mainly to the photochemical oxidation of its ammonia content under the short-wave ultraviolet portion of sunlight occurring at the higher altitudes. This theory receives support from the following considerations.

As there is a seasonal variation of the intensity of solar energy in any one locality, it follows from the author's views that there should be a corresponding

TABLE 9

Seasonal variation of nitric nitrogen in the atmosphere

SEASON	NITRIC NITROGEN PER LITER OF RAIN
	mgm.
Winter	0.30
Spring	1.00
Summer	2.00
Autumn	1.00

variation in the nitrogen content of the atmosphere. This corollary appears to be borne out by experiment.

Miller (11) points out that several results obtained in various localities show higher amounts of nitrates in the summer than in the winter. Russel and Richards (14), summarizing the results of a long-continued series of analyses, shown that there is a marked difference between summer and winter rainfall and that the winter rain is characterized by low ammonia and nitrate content whereas the summer rain is characterized by high ammonia and nitrate content.

Bineau (2) made observations at Lyons, which are given in table 9.

All these results show that the nitric nitrogen content of the atmosphere is maximum in the summer and minimum in the winter.

Figure 2 shows in one curve the variation of the total radiant energy from month to month, and in the other curve, the variation of the so-called ozone[1]

[1] It is not the ozone but the nitric nitrogen, for recent work has shown that no ozone is present in the lower air, and the test employed for estimation of ozone is given readily by oxides of nitrogen.

but really the variation of the nitric nitrogen content of the atmosphere from month to month. It is interesting to note how one curve follows the other. From winter to summer the amount of nitrite is on the rise, while from summer to winter it is on the decline, corresponding to changes in the intensity of sunlight.

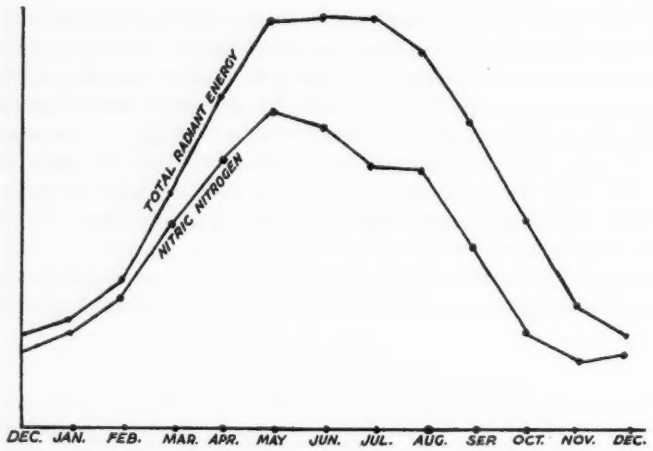


FIG. 2. MONTHLY VARIATIONS OF THE TOTAL RADIANT ENERGY OF THE SUN AND THE NITRIC NITROGEN OF THE ATMOSPHERE

Curves drawn from results of the Radcliffe Observatory, Oxford, vol. 51, p. 214

TABLE 10

*Ammoniacal and nitric nitrogen brought down by rain in various localities**

Data in pounds per acre per annum

LOCALITY	NITRIC NITROGEN	AMMONIACAL NITROGEN	NITRIC N / AMMONIACAL NITROGEN
British Guiana	1.886	1.006	1.874
Barbados	2.443	1.009	2.322
Rothamsted	1.130	2.710	0.419
Kansas	1.060	2.630	0.403
Iceland	0.263	0.802	0.327

* This table is taken from Mellor's comprehensive *Treatise on Inorganic and Theoretical Chemistry*, vol. 8, p. 13.

Hayhurst and Pring (8) find that the proportion of nitric nitrogen is greater at high altitudes than at low altitudes. The ratio of the oxides of nitrogen in the upper air to that in the lower atmosphere was found to be 2.23:1 at 8,500 feet elevation and 1.76:1 at 2,600 feet elevation. This observation is readily explainable on the present photochemical theory, as the proportion of ultraviolet radiation is greater at high than at low altitudes.

As in the tropical countries the length of the day and the intensity of the sun is much greater than in temperate climates, it will be expected that the proportion of nitric nitrogen in the rain of tropical countries will be much higher than that of the rain of temperate climates.

Clarke (3) has compiled the data in table 10 showing the amount of ammoniacal and nitric nitrogen brought down by the rain annually in various localities. The table shows that the ratio of nitric to ammoniacal nitrogen is greater in tropical countries than in the temperate and frigid zones. It will be seen, therefore, that the nitric nitrogen is usually in excess of ammoniacal nitrogen in the rain of tropical countries, but the converse is true of temperate and frigid zones.

SUMMARY

The author has adduced considerable evidence, experimental and otherwise, to show that nitrification in the soil is also partly due to the photochemical action of sunlight. This theory receives added support from the evidence collected to show that the nitrification in the atmosphere is mostly due to the photochemical action of the short-wave ultraviolet portion of sunlight. The author's experiments show that sunlight plays a prominent rôle in the chemistry of soil processes. This important factor has been long overlooked; the author hopes that a clear recognition of this factor will lead to a fundamental modification of our views regarding the mechanism of various material transformations occurring in the soil.

The slow oxidation of ammonia in aqueous solution to nitrite has been shown to take place in transparent silica vessels under the action of the light from a quartz mercury vapor lamp, copper arc, or more slowly in sunlight.

It has also been found that the rate of the oxidation of ammonia in sunlight is considerably increased in the presence of small quantities (as low as 0.1 per cent) of photocatalysts like heated titanium dioxide, aluminum oxide, and zinc oxide. In the presence of these photosensitizers the oxidation also occurs in glass vessels. Ammonium salts can also be thus nitrified, if a basic substance like calcium carbonate is present in the system. Sterilized soil also accelerates the oxidation of ammonia solutions in sunlight.

The oxidation of various complex nitrogenous compounds has also been brought about in sunlight in the presence of the photocatalysts mentioned. Acid amides like acetamide, propionamide, carbamide, or urea are first hydrolyzed photochemically, giving ammonia: and this ammonia is then oxidized to nitrite. Amino acids like glycine, alanine, amino, and succinic acid are first decomposed to ammonia, carbon dioxide, and the corresponding aldehyde. Amines are also oxidized to nitrite.

These experimental results show that nitrification in the soil is at least partly photochemical, taking place without the agency of bacteria under the action of sunlight at the surface of various soil photocatalysts like alumina and titania. There is considerable indirect evidence in favor of this view.

but really the variation of the nitric nitrogen content of the atmosphere from month to month. It is interesting to note how one curve follows the other. From winter to summer the amount of nitrite is on the rise, while from summer to winter it is on the decline, corresponding to changes in the intensity of sunlight.

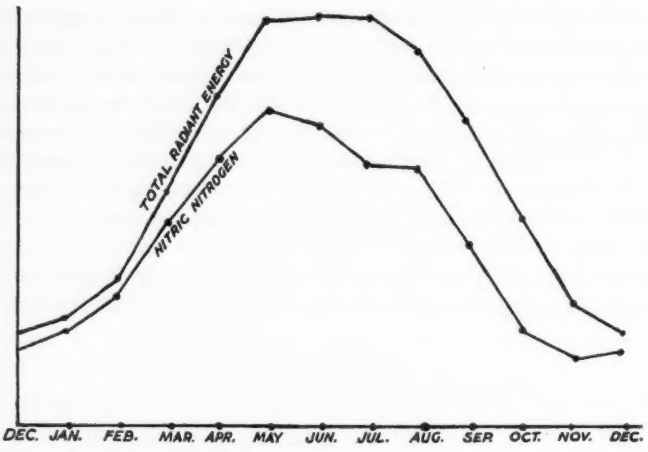


FIG. 2. MONTHLY VARIATIONS OF THE TOTAL RADIANT ENERGY OF THE SUN AND THE NITRIC NITROGEN OF THE ATMOSPHERE

Curves drawn from results of the Radcliffe Observatory, Oxford, vol. 51, p. 214

TABLE 10

*Ammoniacal and nitric nitrogen brought down by rain in various localities**

Data in pounds per acre per annum

LOCALITY	NITRIC NITROGEN	AMMONIACAL NITROGEN	NITRIC N / AMMONIACAL NITROGEN
British Guiana	1.886	1.006	1.874
Barbados	2.443	1.009	2.322
Rothamsted	1.130	2.710	0.419
Kansas	1.060	2.630	0.403
Iceland	0.263	0.802	0.327

* This table is taken from Mellor's comprehensive *Treatise on Inorganic and Theoretical Chemistry*, vol. 8, p. 13.

Hayhurst and Pring (8) find that the proportion of nitric nitrogen is greater at high altitudes than at low altitudes. The ratio of the oxides of nitrogen in the upper air to that in the lower atmosphere was found to be 2.23:1 at 8,500 feet elevation and 1.76:1 at 2,600 feet elevation. This observation is readily explainable on the present photochemical theory, as the proportion of ultraviolet radiation is greater at high than at low altitudes.

As in the tropical countries the length of the day and the intensity of the sun is much greater than in temperate climates, it will be expected that the proportion of nitric nitrogen in the rain of tropical countries will be much higher than that of the rain of temperate climates.

Clarke (3) has compiled the data in table 10 showing the amount of ammoniacal and nitric nitrogen brought down by the rain annually in various localities. The table shows that the ratio of nitric to ammoniacal nitrogen is greater in tropical countries than in the temperate and frigid zones. It will be seen, therefore, that the nitric nitrogen is usually in excess of ammoniacal nitrogen in the rain of tropical countries, but the converse is true of temperate and frigid zones.

SUMMARY

The author has adduced considerable evidence, experimental and otherwise, to show that nitrification in the soil is also partly due to the photochemical action of sunlight. This theory receives added support from the evidence collected to show that the nitrification in the atmosphere is mostly due to the photochemical action of the short-wave ultraviolet portion of sunlight. The author's experiments show that sunlight plays a prominent rôle in the chemistry of soil processes. This important factor has been long overlooked; the author hopes that a clear recognition of this factor will lead to a fundamental modification of our views regarding the mechanism of various material transformations occurring in the soil.

The slow oxidation of ammonia in aqueous solution to nitrite has been shown to take place in transparent silica vessels under the action of the light from a quartz mercury vapor lamp, copper arc, or more slowly in sunlight.

It has also been found that the rate of the oxidation of ammonia in sunlight is considerably increased in the presence of small quantities (as low as 0.1 per cent) of photocatalysts like heated titanium dioxide, aluminum oxide, and zinc oxide. In the presence of these photosensitizers the oxidation also occurs in glass vessels. Ammonium salts can also be thus nitrified, if a basic substance like calcium carbonate is present in the system. Sterilized soil also accelerates the oxidation of ammonia solutions in sunlight.

The oxidation of various complex nitrogenous compounds has also been brought about in sunlight in the presence of the photocatalysts mentioned. Acid amides like acetamide, propionamide, carbamide, or urea are first hydrolyzed photochemically, giving ammonia: and this ammonia is then oxidized to nitrite. Amino acids like glycine, alanine, amino, and succinic acid are first decomposed to ammonia, carbon dioxide, and the corresponding aldehyde. Amines are also oxidized to nitrite.

These experimental results show that nitrification in the soil is at least partly photochemical, taking place without the agency of bacteria under the action of sunlight at the surface of various soil photocatalysts like alumina and titania. There is considerable indirect evidence in favor of this view.

Experiments of several agricultural chemists clearly show that the nitrifying capacity of the soil is maximum in the summer months and minimum in the winter months. This seasonal variation of the nitrate and nitrite content of soils can be successfully explained on the basis of the photochemical view now put forward.

Nitrification in the atmosphere also appears to be due to the photochemical action of sunlight. The monthly variation of the nitric nitrogen content of the atmosphere is closely correlated with the variation of the intensity of sunlight from month to month.

A new method developed by the author for the estimation of small quantities of nitrite has been described. The extreme delicacy and rapidity of the method commend its general use.

APPENDIX

On the non-biological oxidation of nitrite to nitrate

The most important stage in the nitrification process is the one leading to the production of nitrite from ammonia. Even the most powerful oxidizing agents, like chromic acid and potassium permanganate, cannot bring about the oxidation of ammonia to nitrite at ordinary temperatures. But the second stage in the nitrification process, namely, the oxidation of nitrite to nitrate, is easily accomplished. Nitrite easily undergoes oxidation to nitrate by atmospheric oxygen in the presence of acids at ordinary temperatures.

According to Gmelin-Kraut (*Handbuch Anorg. Chem.* 1: 1, 27), Berzelius found a direct oxidation of nitrite to nitrate with air. On the other hand, Matignon and Marchal [*Compt. Rend.* 170: 232 (1920)] were unable to show a direct oxidation in neutral medium. Reinders and Vles [*Rec. Trav. Chim. Pays.-Bas.* 44: no. 1 (1925)] have also arrived at the conclusion that there is no perceptible oxidation of nitrite in neutral or alkaline solution. A weak acid solution of nitrite, however, absorbs oxygen readily. The rate of oxidation of nitrite to nitrate increases with increase in the acidity of the solution. In fact the velocity of the reaction depends on the concentration of free nitrous acid in solution.

It is well known that carbon dioxide can liberate nitrous acid from a nitrite solution, which may easily be demonstrated when a stream of this gas passes through. The acidity of the solution then increases considerably (pH from 8.8 to 5.5). It is clear, therefore, that in the presence of dissolved carbon dioxide the nitrite solution no longer remains alkaline or neutral, but becomes acid. Hence a slow oxidation of the nitrite will follow, because the nitrous acid liberated by carbon dioxide yields nitric acid, which again liberates fresh nitrous acid. In this way we can explain at the same time why Berzelius did notice oxidation in air, while Matignon and Marchal, who worked with great care, were unable to demonstrate a direct oxygen reaction.

From what has been said above, it is clear that a slow oxidation of nitrite to nitrate takes place in the presence of air and carbon dioxide. This reaction is important from the point of soil chemistry; indeed Muntz (quoted in Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 8, section on Biological Fixation of Nitrogen) has shown that nitrites may be oxidized chemically by the joint action of the carbon dioxide and oxygen of the atmosphere. The author has repeated the experiments of Muntz. Twenty cubic centimeters of 0.002 *N* sodium nitrite solution was put into a flask through which a current of pure carbon dioxide and of purified air was bubbled simultaneously for about 8 hours. At the end of this period the amount of nitrite left over was estimated, by the authors' iodometric method. The following are the results:

Volume of 0.002 N nitrite solution taken	*Equivalent amount of 0.002 N hypo solution before treatment*	*Equivalent amount of 0.002 N hypo solution after passing CO_2 and air*
25.0 cc.	25.0 cc.	20.00 cc. after 8 hrs.
20.0 cc.	20.0 cc.	16.20 cc. after 8 hrs.
20.0 cc.	20.0 cc.	15.70 cc. after 9 hrs.

These experiments confirm the findings of Muntz that nitrite undergoes oxidation to nitrate under the joint action of carbon dioxide and air.

It is clear from these results that the oxidation of nitrite to nitrate can take place without the action of bacteria in the presence of carbon dioxide and air; and very likely this reaction takes place normally in the soil.

REFERENCES

(1) BATHAM, H. N., AND NIGAM, L. S. 1930 Periodicity of the nitrate content of soils. *Soil Sci.* 29: 181–190.

(2) BINEAU, A. 1854 *Ann. Chim. et Phys.* (3) 42: 462.

(3) CLARKE, F. W. 1921 The Data of Geochemistry, p. 52. Washington, D. C.

(4) CUTLER, D. W., AND MUKERJI, B. K. 1931 Nitrite formation by soil bacteria, other than Nitrosomonas. *Proc. Roy. Soc.* [London] B 108: 384–394.

(5) GEILMANN 1920 Über die Verbreitung des Titans in Böden und Pflanzen. *Jour. Landw.* 68: 107–124.

(6) GOPALA RAO, G., AND DHAR, N. R. 1931 Photosensitized oxidation of ammonia and ammonium salts and the problem of nitrification in soils. *Soil Sci.* 31: 379–384.

(7) GREEN, H. H. 1914 Nitrification in soil tests. *Centbl. Bakt.* (II) 41: 577–608.

(8) HAYHURST, W., AND PRING, J. N. 1910 Examination of the atmosphere at various altitudes for oxides of nitrogen and ozone. *Jour. Chem. Soc.* 97: 868–877.

(9) JENSEN, C. A. 1910 Seasonal nitrification as influenced by crops and tillage. U. S. Dept. Agr. Bur. Plant. Indus. Bul. 173.

(10) LEMMERMANN, O., AND WICHERS, L. 1920 Über den periodischen Einfluss der Jahreszeit auf den Verlauf der Nitrifikation. *Centbl. Bakt.* (II) 50: 33.

(10a) MEYERHOF, O. 1917 *Pflüger's Arch. Physiol.* 166: 240.

(11) MILLER, N. H. J. 1915 Soils and fertilizers. *Ann. Rpts. Prog. Chem.* [London] 12: 211–233.

(11a) OMELIANSKY, W. *Centbl. Bakt.* (II) 5: 473 (1900); 9: 163 (1902).

(12) PASTEUR, L. 1862 *Compt. Rend. Acad. Sci.* [Paris] 54: 265–270.

(13) PRESCOTT, J. A., AND PIPER, G. R. 1930 Nitrate fluctuations in a South Australian soil. *Jour. Agr. Sci.* 20: 517–531.

(14) RUSSEL, E. J., AND RICHARDS, E. H. 1919 The amount and composition of rain falling at Rothamsted. *Jour. Agr. Sci.* 9: 309–337.

(15) SCHLOSING, T., AND MUNTZ, A. 1877 *Compt. Rend. Acad. Sci.* [Paris] 84: 401; 85: 1018.

(16) SMITH, J. B. 1928 Distribution of nitrates in three layers of fallow soil. *Soil Sci.* 26: 347–350.

(17) WARINGTON, R. 1878, 1879 *Jour. Chem. Soc.* 33: 44 (1878); 35: 429 (1879).

(18) WINOGRADSKY, S. 1890, 1891 The formation of nitrates in the process of nitrification. *Ann. Inst. Pasteur* 4: 213, 257 (1890); 5: 92, 577 (1891).

LAWS OF SOIL COLLOIDAL BEHAVIOR: II. IONIC EXCHANGE WITH HYDROXIDES

A. J. PUGH

New Jersey Agricultural Experiment Station

Received for publication August 21, 1933

The contamination of precipitates by adsorption of substances dissolved in the solution from which they separate is a general phenomenon, but the degree to which various precipitates are contaminated varies widely with different precipitates. The general nature of the process is, however, not known, chiefly because of the widely different viewpoint that occurs between most investigators in this field. Mattson (2) in an investigation of soils and synthetic silicates made an important contribution by correlating the adsorption, both anionic and cationic, with the electrokinetic behavior, and the application of this principle has been extended in this work to hydroxides of the various metals.

Hydroxides are a very important group of compounds, from both the theoretical and the commercial standpoints. Alumina is used as a coagulant in the purification of water supplies, but the chief commercial use of hydroxides is as mordants in the dyeing of fabrics. In general a mordant may be defined as any substance that is adsorbed strongly by the cloth and in turn adsorbs the dye strongly. For this purpose chromium, aluminum, iron, tin, and copper have been used for cotton and wool, while titanium is said to be an extremely good mordant for leather.

The main purpose of this investigation, however, was to determine the influence of pH on the adsorption of anions by the various hydroxides. The adsorption of anions has in the past been confined largely to a determination of the influence of concentration on the degree of adsorption, the influence of pH having been neglected. It has been found that the differential effect of concentration can usually be expressed by the Freundlich adsorption isotherm:

$$\frac{y}{m} = KC^{\frac{1}{p}}$$

where $\frac{y}{m}$ = amount adsorbed per unit of colloid, K and p are constants and C is the final concentration.

Such an equation gives an adequate mathematical expression to the facts, but obscures the nature of the process, as no physical interpretation can be given to it. So many factors enter into the phenomenon of adsorption, such

as the age of the colloid, exchange reactions, and solubility effects, that very little, if any, information can be gained by the use of such a formulation.

THE ISOELECTRIC POINT AND ION EXCHANGE

The composition of the micelle in most colloidal complexes is never known with certainty, as the molecules that polymerize with the formation of colloidal aggregates are many, such as silicates, phosphates, and humates of iron and aluminum in the case of soil colloids. Since we are concerned not so much with their composition, but with their capacity to adsorb and exchange ions, the isoelectric point if characterized by the simultaneous determination of pH gives an extremely important point for a comparison of their properties and exchange reactions (2). When the colloids are regarded as amphoteric electrolytes with one large sluggish ion, the isoelectric point occurs at that pH where the cationic and anionic dissociations are equal and at a minimum.

When an electrodialyzed soil is added to a solution of a neutral salt an exchange acidity is almost invariably developed, for with soils their acid dissociation is much stronger than their basic dissociation and their isoelectric point is always below pH 7.0. If treated with a neutral salt the cation of the salt is exchanged for the hydrion of the colloid, and not the anion of the salt with the hydroxyl of the colloid. Mattson and Hester (4), however, found that if a soil was treated with a salt solution, the pH of which had been adjusted below the isoelectric pH of the colloid, then an exchange alkalinity was developed, the hydroxyl ion being replaced by the anion of the salt.

EXPERIMENTAL

Approximately a liter of the normal solutions of the chlorides of the metals was treated with sodium hydroxide solution, until the isoelectric pH of the colloids, as had previously been determined by cataphoresis, was reached.[1] The pH values at which the various hydroxides are isoelectric are given in table 1.

The floc was separated from the mother liquor by filtration but without washing, the colloid suspended in distilled water and analyzed for the oxide. For the determination of exchange neutrality, an aliquot of the sol was mixed with 100 cc. of the several oxalate solutions in 200-cc. flasks, the total volume in each case being made up to 200 cc. The flasks were shaken at frequent intervals during the day, and the floc was allowed to settle overnight. The "pH after" determination was made on the supernatant liquid with the quinhydrone electrode. A like solution diluted with water instead of with the colloid was used to obtain the "pH before" with the hydrogen electrode. The quantity of oxalate adsorbed was obtained by titrating an aliquot of the supernatant liquid with standard permanganate, and taking the difference of the latter value and the original concentration as the quantity adsorbed. By

[1] Mattson, S. and Pugh, A. J. Unpublished data.

the use of sodium oxalate and oxalic acid of the same concentration, the pH could be varied while the oxalate concentration was kept constant.

ANION ADSORPTION

The adsorption of oxalate and the pH are shown graphically for the various hydroxides in figures 1, 2, 3, 4, and 5. For the stannic, ferric, and chromic hydroxides, the quantity of oxalate adsorbed diminishes consistently with increasing pH of the solution, and in almost all cases there is exchange neutrality with solutions the pH of which is below the isoelectric pH of the colloid and exchange acidity above. Regarding the colloids as amphoteric electrolytes with one sluggish ion permits of a fairly easy interpretation, and the effect is identically the same as has previously been found by Mattson (3) with soils.

Mattson, working with a Nipe soil colloid, discovered that the adsorption of NH_4 from a solution of ammonium chloride took place with increasing pH of the solution and a simultaneous increase in the electronegative charge of the particle. With a decrease in the electronegative charge the adsorption of NH_4 diminished and was accompanied by a lowering of the pH of the ammonium chloride. As the colloid became positively charged the adsorption of

TABLE 1

Isoelectric pH of the hydroxides of the metals prepared from the chlorides

	HYDROXIDE				
	Stannic	Titanic	Ferric	Aluminum	Chronium
pH.....	3.9	4.8	7.1	8.2	8.0

NH_4 became almost negligible but the chlorine adsorption increased. Because of the high salt concentration with these hydroxides, the cataphoretic mobility could not be determined, but the following explanation will make the exchange reactions clear.

Hydroxides are formed by hydrolysis of the chlorides, and as has previously been pointed out in discussing the phenomenon of aging, the bonds must be co-valent, but the co-valencies change into electro-valencies at the isoelectric pH, at two different points in the colloid

$$X - O - H \rightleftarrows [X\,O]^- + H^+$$
$$\rightleftarrows [X]^+ + OH^-$$

and for the oxalate adsorption with the hydroxides of iron, aluminum, and chromium, this is true, as can be seen from the graphs. In an oxalate solution of high pH, the colloid lowers the pH of the solution but increases it if the oxalate solution had originally a low pH. The two dissociations must be equal at the isoelectric point, but because these hydroxides, if leached with a solution of barium acetate of a pH which is identically equal to their isoelec-

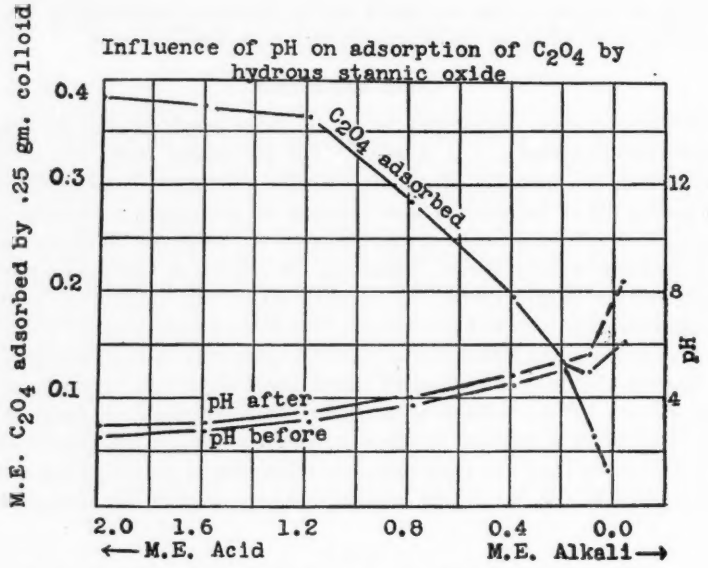


FIG. 1. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

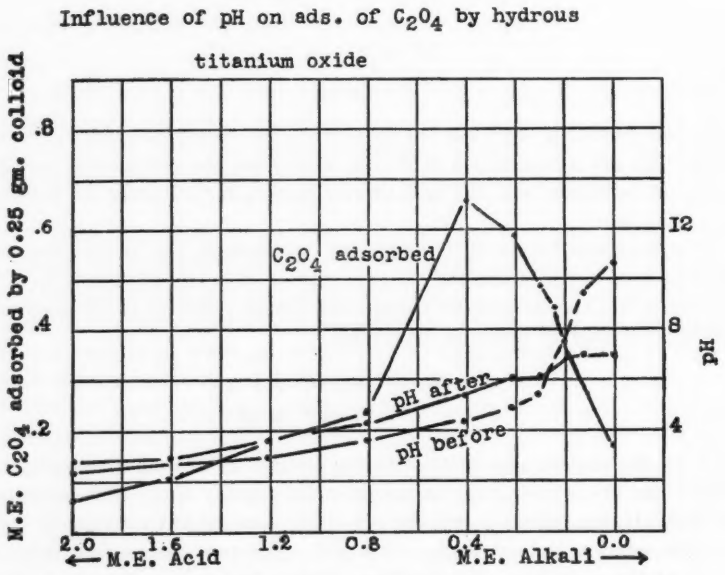


FIG. 2. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

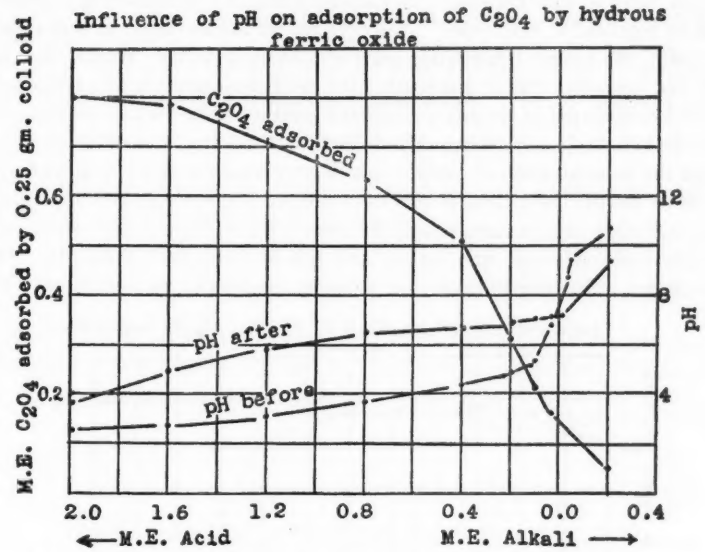


FIG. 3. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

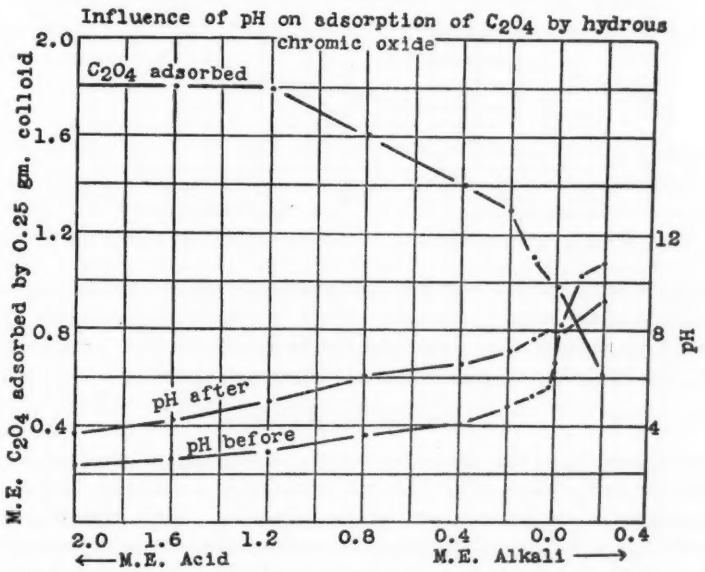


FIG. 4. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

tric pH, have no base exchange, the cationic ionization at the isoelectric point must be regarded as very small. Since the colloid has no charge at the isoelectric point, the anionic dissociation must also be equal to the cationic dissociation, and for both types of dissociation the total dissociation is at a minimum.

The lower the pH of the salt solution the greater will be the anionic dissociation, the hydroxyl ions forming a diffuse layer surrounding the positive micellae. When the concentration of oxalate ions is kept constant at all ranges of pH, the lower the pH the greater will be the ionic exchange of hydroxyl for oxalate ions, and other factors being equal, the greater the adsorption of oxalate ions; but the hydroxyl must first ionize, and this is controlled by the pH. The dissociation of hydroxyl ions is not, however, completely prevented until the

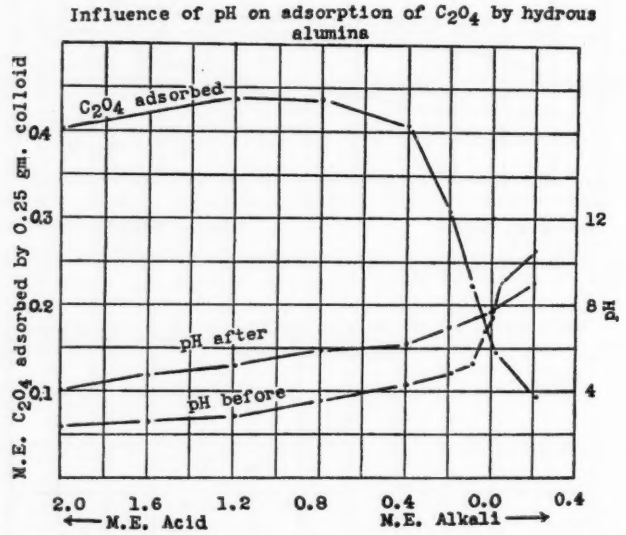


FIG. 5. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

pH of the salt solution is higher than the isoelectric pH, so that there is with oxalate solutions a slight adsorption of $C_2O_4^{=}$ above the isoelectric pH. The amount is, however, very small and hardly significant when working with very dilute solutions of oxalate as used in these experiments.

ADSORPTION AND SOLUBILITY

It has been found that the adsorption phenomena such as described in this paper are purely chemical in character, involving ionic exchange such as the replacement of the hydroxyl ion by the oxalate ion. With increasing ionic concentration the Freundlich adsorption isotherm does fit the adsorption extremely well, and Kolthoff (1) found that purely chemical reactions could be represented in such a manner. It is therefore necessary to derive the isotherm

by the aid of stoichiometry. He does this as follows. To start with a simple case, let us shake a slightly soluble salt, AB, with a solution containing C ions, which is capable of forming the slightly soluble compound AC. For example, let AgBr be shaken with a solution of thiocyanate. The reaction is as follows:

$$AgBr + CNS^- \rightleftarrows AgCNS + Br^-$$

If $K \cdot AgBr$ and $K \cdot AgCNS$ are the solubility products of AgBr and AgCNS, then the concentration of the silver ion is

$$[Br^-] = \frac{K\,[AgBr]}{K\,[AgCNS]} \times [CNS^-] = K_1\,[CNS^-]$$

Now Br^- is the quantity of bromide ion which went into solution and is therefore equal to the quantity of thiocyanate taken out of solution. This is equal to $\frac{x}{m}$ and the concentration of thiocyanate (CNS^-) remaining in solution is equal to the final concentration C.

Substituting in the foregoing equation we have $\frac{x}{m} = K_1\,C$ for monovalent ions. With the displacement of a divalent ion, by two monovalent ions, the equation is $\frac{x}{m} = K_1\,C^2$.

The magnitude of the coefficient K_1 depends on the solubility product of the slightly soluble compounds. With aluminum hydroxide and the adsorption of oxalate, the equation can be represented as follows:

$$Al_n(OH)_x + C_2O_4^- \rightarrow Al_n(OH)_{x-2}\,C_2O_4 + 2\,OH^-$$

but the solubilities of the hydroxide and the compound formed by adsorption of the oxalate are not the same, so that the law of diminishing adsorption with increasing pH does not strictly apply to either titanium or aluminum when oxalate is the ion adsorbed because of the secondary effect of solubility.

The increased solubility could be tested by determining the metallic ion in solution, but analytical difficulties in the absence of micro methods would be very great for small quantities. If another ion could be found which obeyed the law, then we would be safe in assuming that with oxalate adsorption solubility plays a very important part. In order to prove this the simultaneous adsorption of both oxalate and sulfate was studied with alumina and chromium hydroxide.

A quantity of sol was added to 250 cc. of a solution containing equivalent quantities of SO_4^- and $C_2O_4^-$, the pH being varied by using sulfuric acid, sodium sulfate, sodium oxalate, and oxalic acid, all with equivalent concentrations of anions. The total volume in each case was made up to 500 cc., and the pH values before and after were determined colorimetrically. Equilibrium was established by hand shaking at frequent intervals over a period of 3 days.

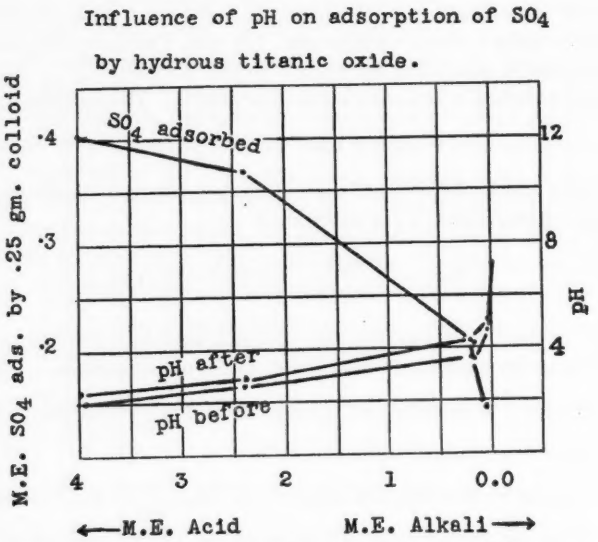


FIG. 6. ORIGINAL CONCENTRATION OF SO_4 4.0 M.E. IN 200 CC.

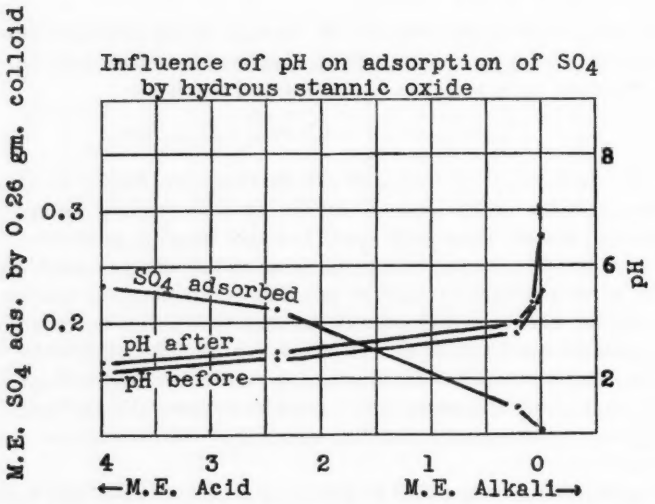


FIG. 7. ORIGINAL CONCENTRATION OF SO_4 4.0 M.E. IN 200 CC.

The oxalate was determined by titration with standard permanganate solution, and the sulfate determined in a separate aliquot by precipitation as barium sulfate in the presence of sufficient hydrochloric acid to prevent the precipi-

tation of barium oxalate. The results are represented graphically in figures 8 and 9.

While the oxalate adsorption still shows the same discrepancy, the sulfate adsorbed decreases consistently with increasing pH, in the same manner as the oxalate adsorption diminished with pH with the hydroxides of tin and iron. At a low pH the $SO_4^=$ is much more strongly adsorbed than the $C_2O_4^=$, but the reverse is true at the higher range of pH. Although it is usual to represent one ion as being more strongly adsorbed than another in colloid chemistry such as $C_2O_4^= > SO_4^=$, these results with hydroxides give no justification for such a procedure. Too many secondary reactions are obscured by such a method of presentation, not the least of which are the solubility effects and the great influence of pH.

With tin and titanium the simultaneous adsorption of both ions was not determined, but the adsorption of sulfate alone was studied. In the dry state neither of these two colloids adsorbs sulfate, but in the sol form there is a considerable adsorption of $SO_4^=$ below the isoelectric pH. The results are shown graphically in figures 6 and 7, and show again that the sulfate obeys the law, although with the oxalate adsorption by titanium, the secondary solubility effects are considerable.

EXCHANGE NEUTRALITY

With chromium, aluminum, and ferric hydroxide the point of exchange neutrality coincides with the isoelectric pH as previously determined. This is true whether the salt used is an oxalate or sulfate salt, and it is also, as has been found by Mattson and Hester, independent of the concentration of either salt or colloid. The figures show that the original concentration of $C_2O_4^=$ used was only 2.05 m.e. in 200 cc. with 0.25 gm. colloid. With the mixed solutions of oxalate and sulfate the concentration of sulfate and oxalate combined was 10 m.e. in 500 cc. with about 0.90 gm. of colloid. In the oxalate adsorption with tin and titanium hydroxide, the point of exchange neutrality does not coincide with the isoelectric pH, because of the comparatively strong buffering action of the oxalate solutions below pH 6.0, but the titanium hydroxide has its point of exchange neutrality at pH 4.8, the same as its isoelectric point, with sulfate solutions. The exchange neutrality determination for tin hydroxide with the sulfate solutions gave considerable difficulties, because of the grave salt errors to which indicators used at a low pH are subject, and the results for tin are subject to considerable error.

The point of exchange neutrality is, as can be easily seen from the graphs, independent of the concentration of either salt or colloid. It is also independent of the age of the colloid, for the cataphoretic mobilities are taken after the precipitates have stood overnight, but the exchange neutrality was determined with these hydroxides after the compounds had aged for over a week, and it occurs at the same pH whether the salt used is an oxalate or a sulfate, or a mixture of both.

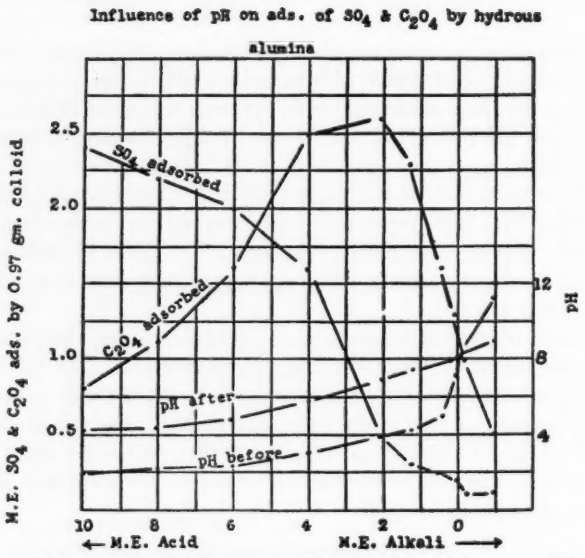


FIG. 8. ORIGINAL CONCENTRATION OF SO_4 PLUS C_2O_4 10.0 M.E. IN 500 CC.

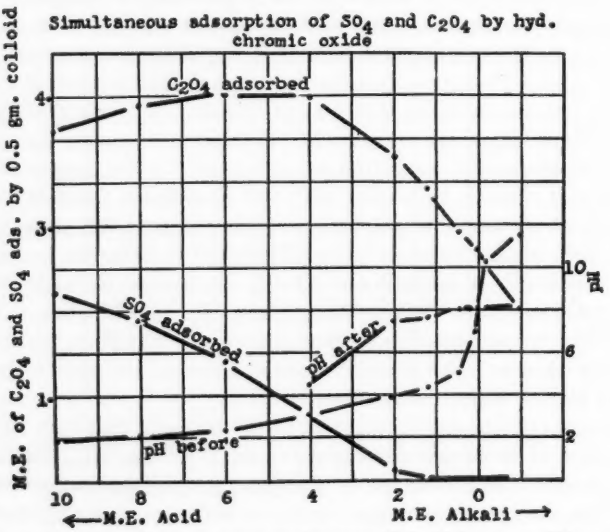
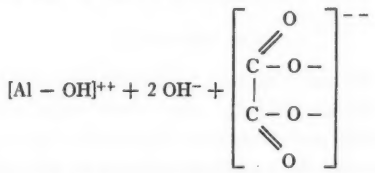


FIG. 9. ORIGINAL CONCENTRATION OF SO_4 PLUS C_2O_4 10.0 M.E. IN 500 CC.

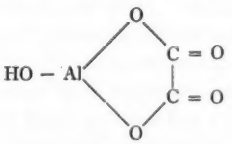
It is important to realize that the point of exchange neutrality as determined with a neutral salt solution refers only to the original compound and not to the new compound formed as a result of the ionic exchange, that is, when the C_2O_4 replaces the OH ion, the adsorption compound will have a new point of exchange neutrality, and an isoelectric point which will occur at a different pH. Substitution of a hydroxyl group by another ion gives, as would be expected, a compound which requires fewer hydroxyl groups to complete its micelle, and hence the isoelectric point of substituted hydroxides occurs at a lower pH.

The substitution of the hydroxyl group by the C_2O_4 ion can be represented most clearly by representing the colloid at the surface as $X — O — H$, which must of course be the case, as the colloids are formed by hydrolysis of the chlorides, the hydroxyl group replacing the chlorine. Taking aluminum hydroxide as an example, we find that the bonds of the anion chloride with the cation aluminum are changed on substitution of the chlorine by hydroxyl from electrovalent to co-valent form (5), and the hydroxide thus formed is isoelectric at pH 8.0. If leached with a solution of barium acetate, pH 8.0, it has no base exchange, but it does have a slight anion exchange, as seen in the graphs. With a solution the pH of which was originally above the isoelectric pH, the colloid dissociates H ions, thus lowering the pH.

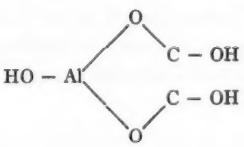
At a pH below its isoelectric pH the aluminum hydroxide would partially dissociate hydroxyl ions, and the oxalate ion would be substituted for it. Representing the ions in solution as follows, with the single bond representing two shared electrons and the double bond four shared electrons, we have:



These would combine to give a compound thus:



which would have a lower isoelectric pH, and it is probable that in a water medium the double bonds on adsorption of hydrions would rearrange to form single bonds:



This is again a co-valent compound, the necessary electrons coming from the lone pair of the oxygen of the oxalate ion. The hydroxyl ions are again at the surface, and the isoelectric point of this compound will also be the point where co-valencies change into electrovalencies, with an acid or alkaline dissociation, depending on the pH of the external medium.

That the point of exchange neutrality is independent of the quantity of adsorption and the nature of the salt can best be understood from this theory. The isoelectric point is that point at which the colloid is largely undissociated and in the co-valent state, with a minimum of the electrovalent form. Hydrions or hydroxyl ions are dissociated if the pH of the salt solution is removed from the isoelectric pH, the character of the dissociation changing, depending on whether the pH of the salt solution is above or below the isoelectric pH of the colloid. Not only the character of the dissociation but also the degree is a function of the pH. Substitution of anions or cations takes place as a secondary ionic reaction, and the amount of cations or anions adsorbed will depend on the concentration of the colloid and the salt, as well as the nature of the colloid and salt, and the solubility of the compound formed. It has been shown previously that the surface bonds are the same whatever the age of the colloid, so that the point of exchange neutrality must be the same whether the colloid be young or old. It is purely a function of the pH, and is that pH at which the dissociation of an amphoteric colloid is at a minimum, and also the pH at which the dissociation changes into an acid or alkaline dissociation, depending on the pH of the external medium.

BASE EXCHANGE

If the isoelectric tin and titanium hydroxides are leached with a normal solution of barium acetate, pH 7.0, they show considerable base exchange capacity, whereas ferric and aluminum hydroxides have none. That ferric and aluminum hydroxides have no base exchange at this pH is due to the fact that pH 7.0 is at or below the isoelectric pH of these compounds and the dissociation of hydrions is negligible. From the graphs it is seen, however, that both ferric and aluminum hydroxides dissociate hydrions if treated with a salt solution the pH of which is above the isoelectric pH. This is definite proof of a potential capacity for base exchange with these compounds, but leaching would have to be made with a salt solution of pH 10 or of a higher pH in order to have an appreciable base exchange. The divalent ions, such as calcium or barium, precipitate hydroxides at such high pH that they cannot be used, whereas the monovalent ions, sodium, potassium, or ammonium, form an exchange compound which is much too soluble with aluminum hydroxide, the so-called aluminates. Unless the pH of the leaching solution is also very carefully defined, it is, however, incorrect to state, as is frequently done, that aluminum hydroxide has no base exchange capacity.

SUMMARY

The influence of pH on the adsorption of oxalate and sulfate ions by various hydroxides has been determined, and the adsorption correlated with the isoelectric pH of the compounds. The lower the pH the greater the anion adsorption, which diminishes with increasing pH and reaches a low value at the isoelectric pH.

With the adsorption of the oxalate ion by aluminum and titanium, a secondary effect of diminished adsorption at low pH values was observed. This did not occur with the sulfate, and hence solubility is an important secondary reaction in ionic exchange reactions with colloids.

The point of exchange neutrality is independent of the concentration or the age of the colloid and of the salt used in so far as determined with solutions of oxalate and sulfate salts of different concentration.

REFERENCES

(1) KOLTHOFF, I. M. 1922 Die Electroadsorption als eine chemische Erscheinung. *Kolloid Ztschr.* 30: 35–50.

(2) MATTSON, SANTE. 1931 Laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311–331.

(3) MATTSON, SANTE. 1931 Laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 343–365.

(4) MATTSON, S. AND HESTER, J. B. 1932 Laws of soil colloidal behavior. X. Exchange neutrality and combining capacity. *Soil. Sci.* 34: 459–482.

(5) PUGH, A. J. 1933 Laws of soil colloidal behavior: XIV. Aging of colloids and base exchange. *Soil Sci.* 37: 403–427.